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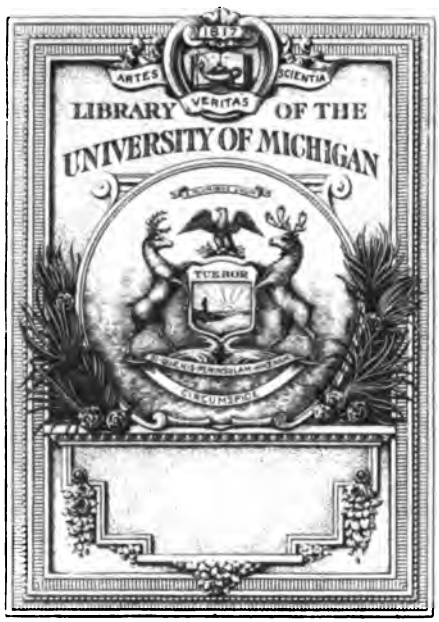
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RICHTER'S ORGANIC CHEMISTRY

ORGANIC CHEMISTRY

OR

CHEMISTRY OF THE CARBON COMPOUNDS

BY

VICTOR VON RICHTER

EDITED BY PROF. R. ANSCHÜTZ AND DR H. MEERWEIN

VOLUME II

CHEMISTRY OF THE CARBOCYCLIC COMPOUNDS

TRANSLATED FROM THE 11TH GERMAN EDITION

BY

E. E. FOURNIER D'ALBE, D.Sc., A.R.C.Sc.

AUTHOR OF "CONTEMPORARY CHEMISTRY," "THE ELECTRON THEORY," ETC.

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PREFACE TO THE ELEVENTH GERMAN EDITION

THE second volume of the present work was published in its last edition in 1905 by me in collaboration with Professor Georg Schroeter. Dr Schroeter, who had also rendered extremely able assistance in the production of the seventh and succeeding editions, was appointed a year ago to the distinguished position of Professor of Chemistry at the Veterinary College in Berlin. Collaboration in the preparation of the present second volume of the treatise was then undertaken by his successor at the Chemical Institute, Dr Hans Meerwein, Assistant Instructor in Organic Chemistry.

RICHARD ANSCHÜTZ.

Since the publication of the second volume seven years have elapsed, during the last few of which the book was out of print. In the course of these latter years the amount of new subject-matter has undergone a remarkable increase. Consequently, the present volume, in comparison with the last edition, has had to be enlarged by more than nine sheets, in spite of the adoption of a larger size of page, as otherwise the whole character of the edition would have been altered.

As in previous editions, a list of the most important interpolations and additions is given below.

Tri-, tetra-, penta-, hepta-, octo-, and *nonocyclic compounds.*—Special attention is called to the ring expansion by the action of nitric acid on cyclo-alkyl methylamine as a new general reaction. The tetramethylene group has been supplemented principally by the inclusion of the simplest examples: cyclobutane, cyclobutene, and cyclobutanone. The simplest saturated, and unsaturated, carbohydrates, with eight-membered carbon rings, are obtained by the transformation of pseudo-pelletierin, and have been very closely examined. By the recognition of the constitution of india-rubber as a polymeric dimethyl, cyclo-octadiene, the group of octocarbocyclic compounds has gained considerably in interest.

The class of nonocarbocyclic compounds has had to be added.

Single-nucleus aromatic substances.—The historical account of the theory of the aromatic compounds has been supplemented at essential points (p. 28).

Special attention is directed to the extremely consistent splitting up of benzene and its homologues by the oxidising action of ozone.

Halogen derivatives of benzene carbohydrates.—Recognition of the fact that the capacity for reaction of aromatically combined halogens

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can be very considerably increased by the addition of finely divided copper or copper salts, has proved of great practical importance.

Nitrogenous derivatives of benzene carbohydrates.—The preparation of optically active dialkyl anilin oxides is worthy of attention.

The behaviour of nitro-diphenylamines in the formation of salts has been more closely examined, and more satisfactory reasons have been given for regarding them as pseudo-acids. As regards new investigations on the diazo-amido-compounds, the preparation of diazo-benzene amide is particularly important. New methods of obtaining diazo-amido-compounds have been discovered. The discovery of two isomeric, differently coloured, series of salts is important, as regards the constitution of amido-azo-compounds, and their salts. Attention is directed to the production of tetraphenyl-hydrazin and its interesting resolving reactions ; see also diphenyl-dihydro-phenazin. The process of reaction in the formation of phenyl-hydrazones, by the action of diazo-benzene salts on aliphatic compounds with easily replaceable hydrogen atoms, has been experimentally elucidated in its individual phases.

The group of aromatic compounds of arsenic has attained greater importance, through the discovery of pharmaceutically valuable substances, such as salvarsan.

Phenols.—The consideration of the nitro-phenols as pseudo-acids has gained in interest by the discovery of a red ester of picric acid. The question of the constitution of the oxy-azo-benzenes has been finally decided in favour of the azo-formula. Reference may also be made to the discovery of cyclic double esters of the phenol-sulpho-acids : sulphonylides.

Quinones.—The discovery of the long-sought o-benzo-quinone should be mentioned in the first place. The nitrogenous derivatives of the quinones have been thoroughly discussed. The investigation of the reactions and constitution of anilin-black by the oxidation of anilin is of the highest importance. Attention may also be called to the remarkable researches regarding the so-called two-nucleus quinones of the diphenyl, naphthalin, and anthracene series.

The nitrogenous derivatives of the oxy-phenyl-paraffin alcohols have been thoroughly discussed, owing to their marked physiological action. Special attention is directed to the analysis and synthesis of adrenalin (p. 370).

Aromatic aldehydes and ketones.—In this group a series of new and, in some cases, easily effected syntheses should be noted. Special attention should be given to the atom displacements in the transformation of the aromatic ethylene glycols, the halogen hydrines, and the ethylene oxides.

Aromatic carbo-acids.—Benzoyl nitrate, benzo-nitrosol acid, benzo-nitrol acid, and benzo-nitrile oxide figure as new carboxyl derivatives of benzoic acid. With reference to the constitution of anthranile, the so-called dianthranilides must be mentioned, as the true bimolecular anhydrides of the anthranile acids. Thiosalicylic acid and its progeny have been much used as the basic products for preparing thio-indigo red.

The discovery of di-iodo-tyrosin in certain species of coral is of physiological importance.

Single-nucleus aromatic substances with unsaturated side chains.—The discovery of the tri-morphism of allo-cinnamic acid, whereby the previously vague isometry of the cinnamic acids may be regarded as explained, is of principal interest in this field.

Hydro-aromatic substances.—Inasmuch as by the smooth method of reduction of aromatic compounds, by means of hydrogen and finely divided nickel, the hydro-aromatic substances have become an easily accessible primary material, this field of research has made remarkable progress, mainly by the use of Grignard's reaction. For determinations of constitution, especially as regards terpenes, the elegant method of oxidation by means of ozone has proved of great service. For terpene chemistry the synthesis of unsaturated hydrocarbons, with semi-cyclic double linking, is of importance. The tetra- and dihydrobenzenes were subjected to a fresh critical study. Extended synthetic investigations with regard to the cyclo-nitrales have finally led to a synthesis of irone, which, however, is not technically valuable. A curious method for the synthesis of different hydro-aromatic substances was discovered in the action of chloroform and alkali on o- and p-alkaline phenols. The production of the optically active forms of 4-methyl-cyclo-hexilidene-acetic acid, in which the asymmetry of the molecule is not caused by the presence of an asymmetric carbon atom, is of technical interest.

Attention might also be directed to the splitting of cyclic ketones by means of sunlight.

Terpenes.—The exceedingly numerous researches made in the entire field of terpene chemistry have necessitated an almost complete reworking, and a partial re-division, in particular of the di-cyclic terpenes. The olefinic terpene group has been enriched by the discovery of ocimene and nerol. The constitutional determinations of the monocyclic terpenes, which may now be regarded as concluded, have been confirmed by numerous syntheses. Thus, dipentene, terpinene, a-phellandrene, sylvestrene, and carvestrene have been obtained in a synthetic manner. A number of analogously composed combinations derived from the terpenes, such as terpinene, terpene, terpinene-cineol, and terpinenol, have ranged themselves alongside of terpin, cineol, and the terpineols. Sabinene and thuyene were associated, by numerous transformations, with terpinene and the terpinenoles. Eucarvone has been examined again, and has been recognised as a heptacarbocyclic combination. The pinene separated from the turpentine oils, has been recognised as a mixture of two linkage-isomeric terpenes, and from these a number of new derived and transformation products are obtained. The transformation of pinene into borneol and isoborneol, or their esters, has been converted into a technically realisable method for the artificial production of camphor from turpentine oil. A fresh and very thorough treatment of camphene has confirmed the Wagner camphene formula; nevertheless, this has raised doubts as to the unity of this terpene. Bornylene, camphane, isocamphane, and santene were the subjects of new and fruitful researches. A series of articles on the behaviour of borneol and isoborneol towards each other, and towards pinene or camphene-chlorohydrate, appear to prove the stereo-isomerism of these combinations. The constitution of fenchone could be accurately ascertained by a series of splitting reactions.

Phenyl-benzenes and phenyl fat carbohydrates.—A series of naturally occurring substances have been recognised as oxybenzo-phenones, and oxybenzylidene-acetophenones, which have hitherto been regarded as phenol esters of protocatechu acid and oxy-cinnamic acid.

Important new observations have been made in favour of regarding the coloured salts of triphenyl-carbinole as quinoid combinations; see also dibenzylidene-acetone.

The benzeïn, rosamin, and phthaleïn classes have been increased by further research.

Prominence should be given to diphenylketene, the most easily accessible, and consequently the most thoroughly examined, factor in this class, rich in reactions.

Amongst the most theoretically important researches which have been made in various directions with excellent results, we may mention those relating to hexaphenyl-ethane, and similar combinations, and their dissociation into the corresponding triaryl-methyls.

The diphenyl-butane group has been enriched by notable papers relating to diphenyl-butadiene and diphenyl-butenin.

Condensed nuclei.—Notice should be taken of the virtual tautomery of anthranol and anthrones, as well as of anthra-hydrokinone and oxanthrone. The amido-anthrakinones have repeatedly shown themselves to be excellent intermediaries for the production of new vat dyes, and so have the dianthrakinonyls and the benzo-anthrones.

Glucosides.—There have been new investigations on certain glucosides related to amygdalin (p. 719).

Natural dye-stuffs.—Much light has been thrown on the complex constitution of cochineal dye.

The above brief review, in the course of which we have only been able to refer to some of the most important recent developments, shows that, in the time which has elapsed, notable progress has been made in nearly all classes of carbocyclic compounds.

RICHARD ANSCHÜTZ.
HANS MEERWEIN.

BONN, *October* 1912.

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A TEXT-BOOK

OF

ORGANIC CHEMISTRY

II. CARBOCYCLIC COMPOUNDS

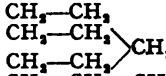
THE methane derivatives, or acyclic carbon compounds, with open carbon chains, dealt with in the first volume of this work, are here followed by organic compounds with closed carbon chains, or carbon rings, and these compounds I call by the name of Carbocyclic Compounds. In contrast with these we have, *e.g.*, the azocyclic compounds with a ring consisting only of nitrogen atoms, such as nitrogen hydride, and its derivatives. The carbocyclic compounds are also called isocyclic compounds, but the latter expression is too comprehensive, since it denotes compounds containing a ring consisting of a number of atoms, of any element. In contradistinction to isocyclic compounds we have the heterocyclic compounds, in which the atoms of several different elements take part in the formation of the ring.

The fundamental carbocyclic hydrocarbons are those with a carbon ring consisting of from three to nine methylene groups. They are isomeric with the olefins, with an equal number of carbon atoms. They are designated either as polymethylenes, in accordance with the number of methylene groups which they contain; or by prefixing an "R" or "R-" to the names of the normal olefins with which they are isomeric ("ring olefins"); or, according to the Geneva resolutions, by the names of the normal paraffins containing an equal number of carbon atoms with the word "cyclo-" prefixed (cyclo-paraffins). The first and third of these designations are to be preferred.

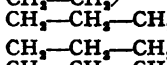
Trimethylene [Cyclopropane]

Tetramethylene [Cyclobutane]

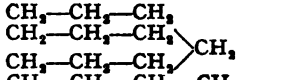
Pentamethylene [Cyclopentane]



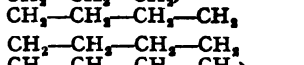
Hexamethylene [Cyclohexane]



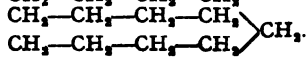
Heptamethylene [Cycloheptane]



Octomethylene [Cyclooctane]



Nonomethylene [Cyclononane]



Hexamethylene is also called hexahydrobenzol, and heptamethylene, suberane. For the nomenclature of ring substances see also B. **29**, 587.

As the paraffins are followed by olefins and diolefins, so the cyclo-paraffins are followed by cyclo-olefin, cyclo-diolefin, and cyclo-triolefin.

Among the carbocyclic structures a special significance attaches to benzol (benzene), the fundamental hydrocarbon of the so-called aromatic substances or benzol derivatives, the most numerous class of organic compounds. If, in accordance with A. Kekulé, we assume in benzol a ring of six carbon atoms linked together in alternate single and double linking—an assumption which the author prefers—benzol is a cyclo-triolefin :

Benzol [Cyclohexatriën] $CH\begin{matrix}/CH & CH\backslash \\ \backslash CH=CH & /\end{matrix}CH$.

By the addition of hydrogen it is possible to convert benzol into hexahydrobenzol, hexamethylene, and cyclo-hexane. A constantly increasing number of transformation products of aromatic compounds are becoming known, which can be referred to dihydro- or tetrahydro-benzol (cyclo-hexadiene and cyclo-hexene), and which, together with the hexamethylene or hexahydrobenzol derivatives, are termed "hydro-aromatic compounds." To these belong many natural products, especially those of the terpene and camphor series. If this system were rigidly followed, every cyclo-paraffin system would be associated with the corresponding cyclo-olefin system having the same number of carbon atoms. But the treatment of the hydro-aromatic substances presupposes a knowledge of the aromatic substances, to such an extent that it is better to deal first with the latter. We therefore treat first of the tri-, tetra-, penta-, hepta-, octo-, and nono-carbocyclic compounds, and afterwards of the hexacarbocyclic compounds.

In many ways the aromatic substances show a peculiar behaviour, different from that of the aliphatic compounds. But the hydro-aromatic compounds, as well as the other known polycarbocyclic compounds, approach in their chemical properties the saturated aliphatic substances, or the unsaturated ones, if there are any double-linked pairs of carbon atoms in the ring. These compounds are therefore called aliphatic cyclic, or alicyclic saturated, and unsaturated, compounds, to distinguish them from the aromatic compounds (B. **22**, 769).

The study of the carbocyclic compounds has shown that the tri- and tetramethylene ring is more easily split than the more stable pentamethylene or hexamethylene ring, while hepta- and octomethylene rings are formed with greater difficulty, and can usually be easily transformed into rings of a smaller number of carbon atoms.

We have met similar phenomena in the formation of some heterocyclic derivatives of aliphatic substances, *e.g.* the lactones, lactames, and dicarboxylic anhydrides (Vol. I.). In the case of the oxy-acids we indicated a scheme of the space-configuration of carbon chains, designed to explain the rare formation of α- and β-lactones, in comparison with the ease with which γ- and δ-lactones are produced. An attempt at explaining the different stabilities of the tri-, tetra-, penta-,

and hexamethylene rings is made in the **tension theory** of A. v. Baeyer (B. **18,** 2278; **23,** 1275). This theory proceeds from the following assumption:—"The four valencies of the carbon atom act in directions joining the centre of a sphere with the corners of an inscribed regular tetrahedron, and therefore form angles of 109° 28′ with each other." These four lines are called axes.

"The direction of attraction can undergo a deflection, but this is accompanied by a tension, increasing with the amount of the latter." The assumption of valency forces acting at an angle is excluded, the amount of deflection being proportional to the tension. "In ethylene the direction of attraction is equally deflected, for both valencies of each carbon atom, until the directions have become parallel. In ethylene the angle of deflection is $\frac{1}{2}(109° 28′)=54° 44′$. In trimethylene, which may be figured as an equilateral triangle, the angle between the axes must be 60°, and the deflection of each must be $\frac{1}{2}(109° 28′-60°)=24° 44′$."

In the same way we obtain the following deflections:

Tetramethylene	$\frac{1}{2}(109° 28′- 90°)$	$= 9° 44′$
Pentamethylene	$\frac{1}{2}(109° 28′-108°)$	$= 0° 44′$
Hexamethylene	$\frac{1}{2}(109° 28′-120°)$	$=- 5° 16′$
Heptamethylene	$\frac{1}{2}(109° 28′-128° 34′)$	$=- 9° 33′$
Octomethylene	$\frac{1}{2}(109° 28′-135°)$	$=-12° 51′$
Nonomethylene	$\frac{1}{2}(109° 28′-140°)$	$=-15° 16′$

This supposes, of course, that the carbon atoms all lie in the same plane, viz. the plane of the ring.

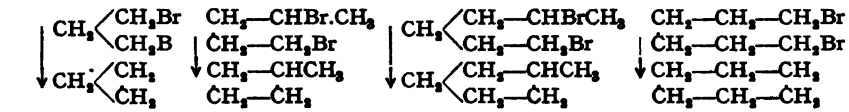
In dimethylene or ethylene the greatest deflection of the direction of action of both valencies has taken place. It has the greatest tension and is the loosest ring, which is easily split up by chlorine, bromine, hydrobromic acid, and iodine. Trimethylene reacts with much greater difficulty. Tetra-, penta-, and hexamethylene rings no longer behave like unsaturated compounds, and are very stable in the presence of halogens, hydrohalogen acids, and potassium permanganate. In harmony with these views, the determination of the heats of combustion of the simplest cyclo-paraffins showed a considerable decrease from tri- to hexamethylene (B. **25,** 496). According to Baeyer's tension theory, the pentamethylene ring should form even more easily than the hexamethylene ring—a conclusion which led to successful attempts to prepare pentamethylene derivatives (B. **28,** 655).

Methods of Ring Formation in Cyclo-paraffin Bodies.

Special importance is attached to the methods by which open carbon chains are converted into closed carbon chains. In accordance with the definition of nuclear syntheses as reactions in which previously unlinked carbon atoms are linked together (Vol. I.), every transformation of an open carbon chain into a closed one must be regarded as a nuclear synthesis. And indeed it is by well-known nuclear synthesis methods applied to suitable aliphatic substances that the closing of rings with formation of cyclo-paraffin bodies has been carried out. The facts in question, already mentioned in divers places in Vol. I., constitute the transition reactions joining the class of paraffins with that

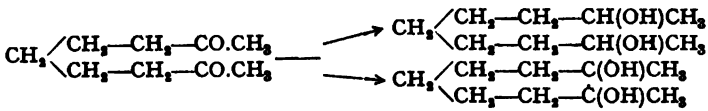
of cyclo-paraffins. The most important items may be briefly enumerated.

1. **Cyclo-paraffins** themselves are produced by the action of sodium or zinc upon dibromo-substituted paraffins, the hydrobromic acid esters of the glycols :

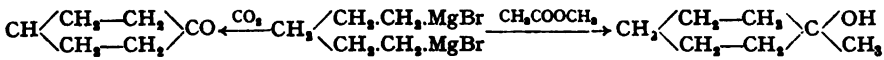


a-Monobromine derivatives of the glutaric acid series yield trimethylene-carboxylic acids even when treated with alcoholic potash.

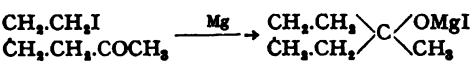
2. **Intramolecular pinacone formation.**—Besides secondary alcohols, the reduction of the ketones yields ditertiary glycols, the pinacones. On reducing diacetyl-pentane we obtain besides an aliphatic disecondary glycol a ditertiary glycol, a cyclic pinacone :



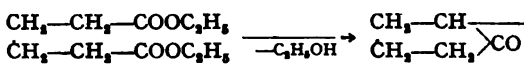
3. **Cyclic syntheses with the aid of metallorganic compounds.**—By treating the di-magnesium compound of the 1, 5-dibromo-pentane with acetic ester we obtain methyl-cyclo-hexanol. Carbonic acid reacts with the formation of cyclo-hexanone :



The synthesis of a tertiary alcohol from a magnesium alkyl iodide and a ketone proceeds intramolecularly in the action of magnesium upon δ-aceto-butyl iodide :

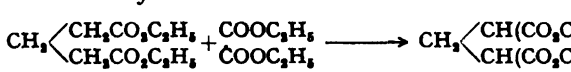


4*a*. **Intramolecular aceto-acetic ester condensation.**—When sodium acts upon adipinic acid ester there is intramolecular condensation corresponding to the formation of acetic ester, and a cyclic β-ketone-carboxylic ester is formed :



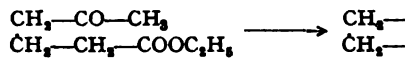
The same behaviour is shown by the esters of the pimelinic acids, which yield β-ketone acid esters with six-membered ring chains.

4*b*. **Oxalo-acetic ester condensation.**—The action of oxalic ester and glutaric acid ester upon sodium ethylate produces diketo-penta-methylene-carboxylic ester :



Similar reactions are shown by β-substituted glutaric acid ester, acetone-dicarboxylic acid ester, methyl-ethyl-ketone, dibenzyl-ketone, etc., with oxalic ester and sodium ethylate.

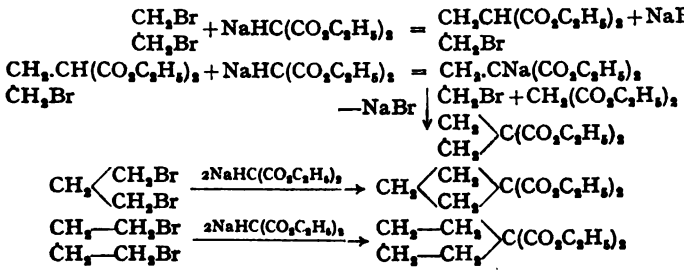
4*c*. **Intramolecular formation of β-diketones.**—γ-acetyl-butyric acid ester is condensed by sodium ethylate to diketo-hexamethylene :



With the same treatment the ε- and ζ-ketonic acid esters yield extra-cyclic β-diketones of the pentamethylene and hexamethylene series.

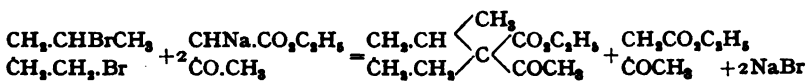
5. **Cyclic syntheses with malonic acid esters, acetic acid esters, etc.** —Through the action of alkylene bromides upon sodium malonic acid esters we obtain cyclo-paraffin acid esters (W. H. Perkin, jun.).

The reaction takes place in three phases :



By introducing the bromination products of olefin-mono- and olefin-dicarboxylic acid esters in the place of alkylene bromides, this reaction has been used for preparing numerous trimethylene derivatives. Cyano-acetic ester behaves like malonic ester (C. 1899, II. 36, 824).

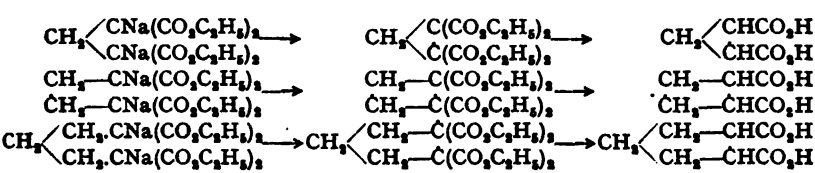
If sodium aceto-acetic ester acts upon 1, 4-dibromo-n-pentane, 1, 2-methyl-acetyl-pentamethylene-carboxylic acid ester is produced :



From 1, 5-dibromo-pentane we correspondingly obtain α-acetyl-hexamethylene-carboxylic ester (B. **21**, 742 ; **40**, 3943).

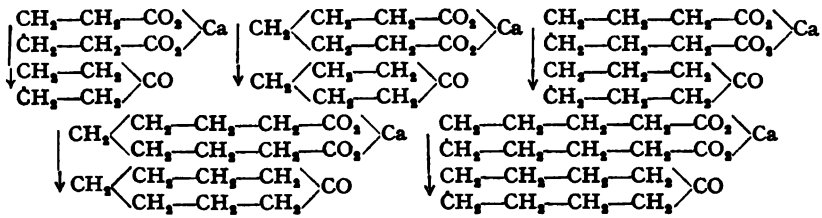
6. From the di-sodium compounds of alkylene-dimalonic esters iodine or bromine extracts the sodium with the formation of a ring, just as iodine converts the sodium aceto-acetic ester into diaceto-succinic ester, and mono-sodium malonic ester into dimalonic ester. From the cyclo-paraffin-tetracarboxylic acids thus produced we may obtain cyclo-paraffin-dicarboxylic acids by splitting off $2CO_2$ (W. H. Perkin, jun.).

Tri, tetra-, penta-, hepta-, octo-, and nonocarbocyclic compounds :



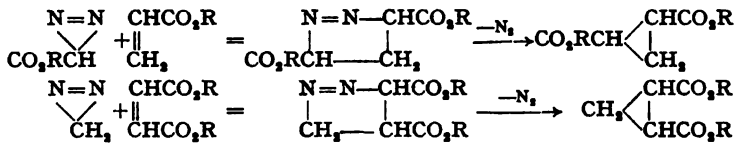
7. **Cyclic ketone formation.**—As the calcium salts of the paraffin-monocarboxylic acids during distillation yield open ketones, so the

calcium salts of some higher normal paraffin-dicarboxylic acids yield during dry distillation cyclic ketones (J. Wislicenus) :



7a. During distillation at ordinary pressures the anhydrides of adipinic and pimelinic acids and their alkyl substitution products split into CO_2 and cyclic ketones (H. G. Blanc; see Vol. I.).

8. **Aliphatic diazo-compounds,** like diazo-methane (Vol. I.) and diazo-acetic ester, add themselves to olefin-mono- and -dicarboxylic esters with the formation of cyclic azo-compounds or pyrazolin compounds, which, by splitting off nitrogen, pass easily into trimethylene-carboxylic acids (E. Buchner) :



Cp. also the condensation of benzol with diazo-acetic ester to isophenyl-acetic or norcaradiene-carboxylic ester.

I.—TRI-, TETRA-, PENTA-, HEPTA-, OCTO- AND NONO-CARBOCYCLIC COMPOUNDS

A number of natural products are closely related to these groups of carbocyclic compounds : carone, eucarvone, pinene, camphor, tropin, ecgonin, pseudo-pelletierin, etc. This group of bodies, therefore, has lately grown in scientific and practical interest.

We may here first give a summary of the physical properties of the simplest cyclo-paraffins (B. **40**, 3981) :

Name.	Melting-point.	Boiling-point.	Sp. G. at 4°.	Refractive Index for D Line.
Cyclopropane .	Gaseous	Approx. −35°	..	..
Cyclobutane .	Liquid	11°–12°	0·7038	1·37520
Cyclopentane .	,,	49°	0·7635	1·40855
Cyclohexane .	+ 6·4°	81°	0·7934	1·4266
Cycloheptane .	−12°	118°	0·8275	1·44521
Cyclooctane .	+11·5°	145·3°–148°	0·850	1·44777
Cyclononane .	..	170°–172°	0·785(?)	1·4328

The molecular refractions determined from the densities and refractive indices indicated agree with those calculated from theory

(see Vol. I., Introduction). It follows that in the cyclo-paraffins the formation of rings has no influence upon the molecular refraction.

A. Trimethylene Group.

Trimethylene (*cyclopropane*) $\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>\!CH_2$ is an easily condensible gas. It is obtained from trimethylene bromide with the aid of sodium (Freund, 1882), or of alcohol and zinc dust (B. **20,** R. 706; *J. pr. Ch.* 2, **7,** 512). It may combine with bromine, especially in the presence of HBr acid, whereby chiefly trimethylene bromide $CH_2Br.CH_2.CH_2Br$ is produced, or with hydriodic acid, forming n-propyl iodide, but it does so with greater difficulty than propylene. At a red heat it transforms itself into propylene (B. **29,** 1297; C. 1899, I. 925, II. 287). In the presence of finely divided nickel, hydrogen reduces it to propane already at 80° (B. **40,** 4459). MnKO solution does not oxidise trimethylene in the cold (B. **21,** 1282).

Concerning the difference in the heats of formation of trimethylene and propylene, see C. 1899, II. 801.

Methyl-trimethylene, b.p. 4° (B. **28,** 22; C. 1902, I. 1277); **1, 1-Dimethyl-trimethylene** b.p. 21° (C. 1899, I. 254; 1900, II. 1069); **1, 1, 2-** and **1, 2, 3-Trimethyl-trimethylene** (B. **34,** 2856); **Vinyl-trimethylene** $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!CHCH=CH_2$, b.p. 40°, D 0·73, are produced in a peculiar reaction by the action of alcohol and zinc dust on the tetra-bromate of penta-erythrite (see Vol. I.); by MnKO it is oxidised to glycol $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!CH\!-\!\begin{matrix}CHOH\\|\\CH_2OH\end{matrix}$, which, by further oxidation with dilute HNO_3, yields α-oxy-glutaric acid; with Br it forms a dibromide, which, on treating with lead oxide, yields keto-pentamethylene (B. **29,** R. 780; C. 1897, II. 696; also C. 1898, II. 475, footnote); with N_2O_3 it gives a pseudo-nitrosite, m.p. 145°, from which on reduction, besides diamine $C_5H_8(NH_2)_2$, b.p. 180°–185°, cyclo-butanone is formed (B. **41,** 915). Concerning another interpretation of vinyl-trimethylene, see B. **40,** 3884.

Dimethyl-methylene-trimethylene $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>\!C=C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$ (?), b.p. 70°–71°, is produced from dimethyl-trimethylene-carbinol on boiling with acetic anhydride (C. 1905, II. 403; 1909, I. 1859).

Monochloro-trimethylene, b.p. 43° (B. **24,** R. 637).

Dichloro-trimethylene, b.p. 74° (B. **25,** 1954).

Amino-trimethylene $(C_3H_5)NH_2$, b.p. 49°, from trimethylene-carboxylic amide with KOBr (C. 1901, II. 579). Miscible with water in all proportions. Smells like propylamine. With nitrous acid it yields allyl alcohol, with splitting of the ring (C. 1905, I. 1704).

Trimethylene-methylamine $(C_3H_5)CH_2NH_2$, b.p. 86°, from trimethylene-carboxylic nitrile by reduction. Gives with nitrous acid trimethylene-carbinol and cyclo-butanol, with expansion of the ring (B. **40,** 4393)

Trimethyl-carbinol $(C_3H_5)CH_2OH$, by the reduction of trimethylene-carboxylic ester with Na and alcohol (B. **40,** 4397). With concentrated HBr it passes into 1, 3-dibromo-butane (C. 1908, I. 818).

Trimethylene-ethyl-carbinol, b.p. 14°.

Trimethylene-isopropyl-carbinol, b.p. 151°.

These two are obtained by reduction of the corresponding ketones.

Trimethylene-dimethyl-carbinol $(C_3H_5)C(CH_3)_2OH$, by treating $Mg(CH_3)I$ with acetyl-trimethylene or trimethylene-carboxylic ester; chloride, b.p. 132°; bromide, b.p. 152°. By oxalic acid it is isomerised, with splitting of the ring, to dimethyl-tetramethylene oxide $CH_3—C(CH_3)_2\rangle O$ $CH_2——CH_2/$ (B. **84,** 3887).

Trimethylene-diethyl-carbinol $(C_3H_5)C(C_2H_5)_2OH$, b.p. 158°.

Trimethylene-methyl-ethyl-carbinol $(C_3H_5)C(CH_3)(C_2H_5)OH$, b.p. 141° (C. 1909, I. 1859).

Trimethylene-aldehyde $CH_2\langle CH_2\rangle CH.CHO$, b.p. 98°, by oxidation of trimethylene-carbinol with chromic acid.

Acetyl-trimethylene $CH_2\langle CH_2\rangle CH.COCH_3$, b.p. 113°:

1. From aceto-propyl-bromide with ejection of HBr by KOH (C. 1898, II. 474).

2. From acetyl-trimethylene-carboxylic acid by heating.

3. By the action of $Hg(CH_3)I$ upon trimethylene cyanide. The three-ring is split up by mineral acids. For homologous ketones see C. 1909, I. 1859.

Trimethylene-carboxylic acids (A. **284,** 197) are obtained by the general methods of ring formation 5, 6, and by method 8, which only leads to trimethylene-derivatives (p. 6). From those trimethylene-polycarboxylic acids which contain two carboxyls bound with one carbon atom, we obtain the carboxylic acids poorer in carboxyl by splitting off CO_2. Certain peculiar phenomena of isomerism (cis- and trans-forms) are attributed to the position of the carboxyls on the same side, or on different sides, of the trimethylene plane, as in the case of the isomerisms of the tri-thio-aldehydes (Vol. I.).

Trimethylene-carboxylic acid $C_3H_5CO_2H$, m.p. 18°, b.p. 183°, is isomeric with crotonic acid. The trimethylene ring is split by bromine with formation of α,γ-dibromo-butyric acid (C. 1909, II. 1130). Its nitrite, b.p. 118°, has been obtained by distilling γ-chloro-butyro-nitrile over KOH; ethyl ester, b.p. 134°; chloride, b.p. 121°; amide, m.p. 124° (C. 1901, II. 579; 1902, I. 913).

Trans-phenyl-trimethylene-carboxylic acid $C_6H_5CH\langle\begin{matrix}CH—COOH\\|\\CH_2\end{matrix}$, m.p. 105°, has been obtained by method 8, by addition of diazo-acetic ester to styrol (*q.v.*). It was successfully disintegrated to cis-trans-trimethylene-1, 2-dicarboxylic acid.

2, 2-Dimethyl-trimethylene-carboxylic acid $(CH_3)_2C\langle\begin{matrix}CHCOOH\\|\\CH_2\end{matrix}$, b.p. 100°, smells strongly of butyric acid. The ester, b.p. 90°, is formed by separation of HBr from the 3, 3-dimethyl-γ-bromo-butyric acid ester (C. 1907, II. 897).

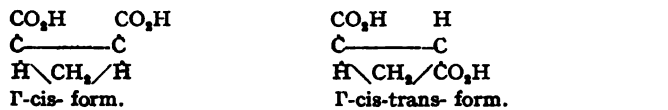
Trimethylene-1, 1-dicarboxylic acid (*vinaconic acid*) $CH_2\langle CH_2\rangle C(CO_2H)_2$, m.p. 140° (see method 5, p. 5). With HBr this passes into brom-ethyl-malonic acid $CH(CO_2H)_2BrCH_2CH_2$. It also takes up bromine

(B. **18**, 3314), but is not affected by HNO_3, $MnKO_4$, or nascent hydrogen (B. **23**, 704; **28**, 8). With Na-malonic ester the ester of vinaconic acid condenses to butane-tetracarboxylic ester, and thus behaves quite like α, β-olefin-carboxylic ester (see Vol. I. and B. **28**, R. 464). Concerning the constitution of vinaconic acid and the homologous methyl-vinaconic acid, see A. **294**, 89.

1, 1-Cyano-trimethylene-carboxylic acid, m.p. 149°, from sodium-cyan-acetic ester and ethylene bromide (C. 1899, II. 824).

Acetyl-trimethylene-carboxylic ester $CH_2\!<\!\begin{matrix}CH_2\\CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}COCH_3\\COOC_2H_5\end{matrix}$, b.p. 195°, from sodium-aceto-acetic ester and ethylene bromide (B. **17**, 1440).

Trimethylene-1, 2-dicarboxylic acid is known in two isomeric forms, distinguished as cis- and cis-trans- or trans- forms (A. **245**, 128):



Γ-cis- form. Γ-cis-trans- form.

Cis-trimethylene-1, 2-dicarboxylic acid, m.p. 139°; anhydride, m.p. 59°, is obtained from tr-1, 2-tri- and -1, 2-tetracarboxylic acid by heating. Cis-trans-trimethylene-1, 2-dicarboxylic acid, m.p. 175°, from monobromo-glutaric acid ester with alcoholic caustic potash (C. 1900, I. 284). It has been separated into two optically active components by means of its quinine salt, like the cis-trans-trimethylene-1, 2, 3-tricarboxylic acid described below (B. **38**, 3112). Its methyl ester, b.p. about 210°, is obtained from acryl-diazo-acetic ester by method 8, besides glutaconic acid ester; and from fumaric acid ester with diazo-methane (B. **27**, 1888; **28**, R. 290).

Cis-phenyl-trans-2, 3-trimethylene-dicarboxylic acid $C_6H_5CH\!<\!\begin{matrix}CHCOOH\\CHCOOH\end{matrix}$, m.p. 175°; anhydride, m.p. 134°; from α-bromo-benzylidene-bis-malonic ester with alcoholic ammonia, or by adding diazo-acetic ester to cinnamic-acid ester (B. **36**, 3774; *J. pr. Ch.*, 2, **75**, 490).

Trimethylene-1, 2-tricarboxylic acid $CH_2\!<\!\begin{matrix}C(CO_2H)_2\\CHCO_2H\end{matrix}$, m.p. 187°, by disintegration. Its ethyl ester, b.p. 276°, from α, β-dibromo-propionic-acid ester (B. **17**, 1187), and from α-brom-acrylic ester with Na-malonic-acid ester by method 5 (B. **20**, R. 140, 258).

Sym. trimethylene-1, 2, 3-tricarboxylic acid $CO_2HCH\!<\!\begin{matrix}CHCO_2H\\CHCO_2H\end{matrix}$, cis-form, m.p. 150°–153°; cis-trans-form, m.p. 220°; anhydride, m.p. 187°, b.p. 265°. The cis-acid is obtained from the 1, 2, 3-tetracarboxylic acid (B. **17**, 1652), the cis-trans-acid from fumaric-acid-diazo-acetic ester (B. **23**, 2583). The latter acid is also obtained from the oxidation of isophenyl-acetic or norcaradiene-carboxylic acid (B. **27**, 868).

Trimethylene-1, 2-tetracarboxylic acid $CH_2\!<\!\begin{matrix}C(CO_2H)_2\\C(CO_2H)_2\end{matrix}$ passes at 200° into the anhydride of the cis-1, 2-dicarboxylic acid. Its ethyl ester, m.p. 43°, $b.p._{12}$ 187°, is obtained from method 6 (B. **23**, R. 241).

Trimethylene-1, 2, 3-tetracarboxylic acid $(CO_2H)_2C\!<\!\begin{matrix}CHCO_2H\\CHCO_2H\end{matrix}$ passes at 95°–100° into cis-1, 2, 3-tricarboxylic acid. Its ethyl ester,

b.p. 246°, from dibromo-succinic ester by method 5. The cis-1, 2,-trans-1, 3 acid decomposes at 196°–198° (B. **28**, R. 290).

1, 1-Dimethyl-trimethylene-2, 3-dicarboxylic acid, *caronic acid* $(CH_3)_2C\langle{}^{CHCO_2H}_{CHCO_2H}$, trans-form, m.p. 213°, passes on heating with acetic anhydride into the cis-form, m.p. 176°. The anhydride of the cis-form melts at 55°. The caronic acids are obtained by oxidation with MnO_4K from carone (see Terpene ketones), which therefore contains a trimethylene ring. Synthetically, the caronic acids have been obtained from α-bromo-ββ-dimethyl-glutaric-acid ester with alcoholic potash (C. 1899, I. 522). By heating with HBr the caronic acids are easily transformed into terebinic acid (*q.v.*). On heating $\alpha\alpha_1$-dibromo-ββ-dimethyl-glutaric ester with alcoholic potash we obtain etho-oxy-caronic acid $(CH_3)_2C\langle{}^{C(OC_2H_5)CO_2H}_{CHCO_2H}$, m.p. 138° (C. 1901, II. 110).

1, 2-Dimethyl-trimethylene-2, 3-dicarboxylic acid, m.p. 154°, is identified with the acid the ester of which is obtained with PCl_5 from oxy-trimethyl-succinic ester (C. 1908, I. 627).

The **1, 1-dialkyl-2, 3-dicyano-trimethylene-2, 3-dicarboxylic acids** have been obtained in considerable numbers in the form of imides of the general formula $\begin{matrix}R\\R_1\end{matrix}\rangle C\langle{}^{C(CN)—CO}_{C(CN)—CO}\rangle NH$, from the corresponding dialkyl-dicyano-bromo-glutarimides (C. 1899, II. 439; 1901, I. 57).

Trimethylene-tricyano-tricarboxylic-acid ester $\begin{matrix}ROCOC(CN)\\ROCOC(CN)\end{matrix}\rangle C\langle{}^{CN}_{COOR'}$ m.p. 119°, is formed by the action of bromine or iodine upon sodium-cyano-acetic ester in ether; on saponification it yields trimethylene-tetra- and then -1, 2, 3-tricarboxylic acid (B. **33**, 2979).

Methyl-cyclo-propene-dicarboxylic acid $CH_3CH\langle{}^{C(CO_2H)}_{C(CO_2H)}$, m.p. 200°, see B. **26**, 750.

B. Tetramethylene Group.

For obtaining tetramethylene compounds the ring formation methods 1, 5, and 6 are used.

Tetramethylene-cyclo-butane $\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}$, b.p. 11°–12°, D_4^0 0·7038, is obtained by reducing cyclo-butene with Ni and H at 100°; at higher temperatures butane is also produced, with splitting of the ring. It possesses a very feeble odour, and burns with a luminous flame. In the cold it is stable in the presence of bromine and concentrated HI.

Methyl-tetramethylene $\begin{matrix}CH_2—CHCH_3\\CH_2—CH_2\end{matrix}$, b.p. 39°–42°, method 1, p. 4.

Cyclo-butene $\begin{matrix}CH_2—CH\\CH_2—CH\end{matrix}$, easily condensible gas of b.p. 1·5°–2°, D_4^0 0·733, generated together with $\Delta^{1\cdot3}$-butadiene during dry distillation of cyclo-butyl-trimethyl-ammonium hydroxide. Adds bromine, forming 1, 2-dibromo-cyclo-butane, $b.p._{24}$ 69°, m.p. —2°, which, with KOH, splits off HBr and passes into *bromo-cyclo-butene*. This is an oil of penetrating odour, b.p. 92°, which oxidises to succinic acid. With bromo-cyclo-butene as a starting-point, a number of bromo-substitution products of cyclo-butane have been prepared. Thus it combines with HBr to **1, 1-dibromo-cyclo-butane** (I.), b.p. 158°, and with Br to **1, 1, 2-tribromo-cyclo-butane** (II.), $b.p._{19}$ 109°. This gives, with alcoholic

KOH, **1, 2-dibromo-cyclo-butene** (III.), b.p. 155°, distinguished by a great faculty for polymerisation. With $KMnO_4$ it oxidises to succinic acid, and combines with Br to form **1, 2-tetra-bromo-cyclo-butane** (IV.), m.p. 126°, which, on further bromination, yields **pentabromo-cyclo-butane** $C_4H_3Br_5$, b.p.$_{19}$ 175°–185°, and **hexabromo-cyclo-butane** $C_4H_2Br_6$, m.p. 186·5°, which is remarkable for its ease of crystallisation (B. **40**, 3979).

(I.) (II.) (III.) (IV.)

$$\begin{matrix}CH_2—CBr\\CH_2—CH\end{matrix} \longrightarrow \begin{matrix}CH_2—CBr_2\\CH_2—CH_2\end{matrix} \quad \begin{matrix}CH_2—CBr_2\\CH_2—CHBr\end{matrix} \longrightarrow \begin{matrix}CH_2—CBr\\CH_2—CBr\end{matrix} \longrightarrow \begin{matrix}CH_2—CBr_2\\CH_2—CBr_2\end{matrix}$$

The name *dimethyl-methylene-tetramethylene* $\begin{matrix}CH_2—C=C(CH_3)_2\\CH_2—CH_2\end{matrix}$, b.p. 100°–102°, is given to the hydrocarbon generated from the bromide of dimethyl-tetramethylene-carbinol by splitting off HBr. On reduction with HI it passes into 1, 3-dimethyl-pentamethylene.

Oxy-tetramethylene, *cyclo-butanol* C_4H_7OH, b.p. 123°, from amido-tetramethylene by the action of HNO_2, and by electrolysis of potassium tetramethylene-carboxylate (B. **40**, 2594, 4962).

Amido-tetramethylene $C_4H_7.NH_2$, b.p. 81°, arises from the amide of tetramethylene-carboxylic acid with bromine and an alkali (B. **40**, 4745).

Tetramethylene-methylamine $\begin{matrix}CH_2.CH.CH_2NH_2\\CH_2.CH_2\end{matrix}$, b.p. 110°, by reduction of tetramethylene-cyanide, gives, with HNO_2, a mixture of **tetramethylene-carbinol** $C_4H_7.CH_2OH$, and **cyclo-pentanol** $C_5H_9.OH$.

Tetramethylene-carbinol $C_4H_7.CH_2OH$, b.p. 142°, by reduction of tetramethylene-carboxylic ester with Na and alcohol; bromide, b.p. 137°–139° (B. **40**, 4959).

Tetramethylene-methyl-carbinol $C_4H_7.CH(OH)CH_3$, b.p. 144°, by reduction of tetramethylene-methyl-ketone.

Tetramethylene-dimethyl- and **diethyl-carbinol,** b.p. 147° and 188° respectively, by the action of $Mg(CH_3)I$ and $Mg(C_2H_5)I$ on tetramethylene-carboxylic ester (C. 1905, II. 761; 1908, II. 1342).

Tetramethylene-diethyl-glycol $[C_4H_7C(OH)C_2H_5]_2$, m.p. 95°, by reduction of tetramethylene-ethyl-ketone.

Keto-tetramethylene-cyclo-butanone $\begin{matrix}CH_2—CO\\CH_2—CH_2\end{matrix}$, b.p. 99°, D_0^0 0·9548, generated (1) by action of bromine and alkali on α-bromo-tetramethylene-carboxylic amyl; (2) during boiling of 1, 1-dibromo-butane with lead oxide and water. Nitric acid oxidises it to succinic acid (C. 1908, I. 123).

Tetramethylene-methyl- and **ethyl-ketone,** b.p. 135° and 145°, from the carboxyl chloride with zinc alkylene (B. **25,** R. 371), or from the amide with $Mg(CH_3)I$ (B. **41,** 2431).

Di-tetramethylene-ketone $(C_4H_7)_2CO$, b.p. 205°, from the calcium salt of carboxylic acid.

Dimethyl- and **diethyl-tetramethylene-ketone** $\begin{matrix}C_2H_5CH—CO\\CH_3—CHC_2H_5\end{matrix}$, m.p. 45°–120° and 160°–165°. This constitution is ascribed to substances obtained during distillation of Ba salts of $\alpha\alpha_1$-dimethyl- and diethyl-glutaric acid (C. 1897, II. 342).

1, 3-Dimethyl-2, 4-diketo-tetramethylene $\begin{matrix}CH_3CH—CO\\CO—CHCH_3\end{matrix}$, m.p. 135°,

by saponification and rejection of CO_2 from the corresponding carboxylic-acid ester, on boiling with bartya water.

1, 1, 3, 3-Tetramethyl-2, 4-diketo-tetramethylene $\begin{matrix}(CH_3)_2C\text{——}CO\\ CO\text{—}C(CH_3)_2\end{matrix}$, m.p. 116°, obtained by rejection of HCl from iso-butyryl chloride. Also by action of molecular silver on bromo-iso-butyryl bromide. In both cases we must assume the formation of dimethyl-ketene (see Vol. I.), which easily polymerises to tetramethyl-2, 4-diketo-tetramethylene. Its odour recalls both menthol and camphor, and it has the great volatility of these compounds.

Dioxime, m.p. 281° (B. **39,** 970).

Tetramethylene-carboxylic acid $C_4H_7CO_2H$, b.p. 194°, smells like the fatty acids, and is generated from 1, 1-dicarboxylic acid; on reduction by HI it yields n-valerianic acid, with splitting of the ring (C. 1908, II. 1342). Ethyl ester, b.p. 160°; chloride, b.p. 142°; anhydride, b.p. 160°; amide, m.p. 130°; nitrite, b.p. 150° (B. **21,** 2692; C. 1899, II. 824).

Tetramethylene-1, 1-dicarboxylic acid melts at 155°, passing into monocarboxylic acid. Its ethyl ester, b.p. 224°, by method 5, p. 5; nitrile ester, b.p. 214°, from trimethylene bromide, and sodium cyan-acetic ester (C. 1899, II. 824; 1905, II. 761).

Cis-tetramethylene-1, 2-dicarboxylic acid, m.p. 137°, from tetracarboxylic acid. Anhydride, m.p. 77°, b.p. 271° (B. **26,** 2243). Heating with HCl to 190° produces the trans-acid, m.p. 131° (B. **27,** R. 734). By bromination with Br and P, 1, 2-dibromo-tetramethylene-dicarboxylic acid is produced; and its ester, on treating with alcohol and KI, passes into the ester of cyclo-butene-dicarboxylic acid $\begin{matrix}CH_2\text{—}CO_2H\\ CH_2\text{—}CO_2H\end{matrix}$, m.p. 178°. The latter easily yields an anhydride (*J. Ch. Soc.* **65,** 950).

Tetramethylene-1, 3-dicarboxylic acid, cis-form, m.p. 136°; anhydride, m.p. 51°; trans-form, m.p. 171°, have been obtained from the products of the action of formaldehyde upon malonic ester, and from α-chloro-propionic-acid ester, with the aid of Na alcoholate (C. 1898, II. 29). Also produced by boiling β-methoxy-methyl-malonic ester with concentrated HCl with the loss of two molecules of methyl alcohol, by saponification, and CO_2-rejection, from the tetra-carbo-ester first formed (C. 1909, I. 152):

$$\begin{matrix}CH_3O\text{—}CH_2\text{—}CH(COOR)_2\\ +\\ (ROCO)_2CH\text{—}CH_2\text{—}OCH_3\end{matrix} \longrightarrow \begin{matrix}CH_2\text{—}C(COOR)_2\\ |\quad\quad|\\ (ROCO)_2C\text{——}CH_2\end{matrix}$$

Tetramethylene-1, 2-tetracarboxylic acid, m.p. 145°–150°, by transformation into cis-1, 2-dicarboxylic acid. Its ester is formed by method 6, p. .

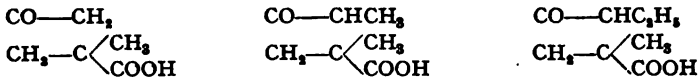
Diacetyl-tetramethylene-dicarboxylic ester by method 6, p. 5 (B. **19,** 2048).

Keto-tetramethylene-tricarbo-esters, such as:

$$\begin{matrix}CO\text{—}CHCOOR\\ |\quad\quad|\\ ROCOCH\text{—}C\langle^{CH_2}_{COOR}\end{matrix} \qquad \begin{matrix}CO\text{—}C\langle^{CH_2}_{COOR}\\ |\quad\quad|\\ ROCOCH\text{—}C\langle^{CH_2}_{COOR}\end{matrix} \qquad \begin{matrix}CO\text{—}C\langle^{C_2H_5}_{COOR}\\ |\quad\quad|\\ ROCOCH\quad C\langle^{CH_2}_{COOR}\end{matrix}$$

are formed by condensation of Na-malonic esters, or methyl and ethyl

malonic esters, with citraconic ester in alcoholic solution, in which process probably the tetracarboxylic esters first formed with open chains undergo cyclic aceto-acetic ester condensation. By saponification with HCl two carbox-ethyl groups are split off the above substances, and the following 1-keto-tetramethylene-3-carboxylic acids are formed (B. **33**, 3751) :



1, 3-Dimethyl-2, 4-diketo-tetramethylene-carboxylic ester $CO{-}C(CH_3){-}COOC_2H_5$, m.p. 133°–135°, has been obtained by the action of concentrated sulphuric acid upon sym. dimethyl-acetone-dicarboxylic ester. By alkalies the ring is easily split again (B. **40**, 1604).

Diethyl-diketo-tetramethylene-dicarboxylic ester, $C_2H_5OCO\,C(C_2H_5)(CO){-}CO{-}C(C_2H_5)(COOC_2H_5)$, b.p.$_0$ *ca.* 113°–116°, is identified with the dimeric ethyl-ketene-carboxylic ester. During distillation at ordinary pressures it is depolymerised. Anilin also splits the molecule, forming ethyl-malonic-ester anilide (B. **42**, 4908).

Tetramethylene-1, 3-diglyoxylic acid $CO_2HCOCH.CH_2$ / $CH_2CH.CO.CO_2H$, m.p. 240°, produced by condensation of tartaric acid and paraformaldehyde with concentrated H_2SO_4. Decomposes into ethylene and oxalic acid by heating with alkalies, and, on further heating with H_2SO_4, it passes into a dilactone (B. **29**, 2273).

By polymerisation of olefin and acetylene carboxylic acids, we sometimes obtain substances with a four-membered carbon ring :

Diphenyl-tetramethylene-dicarboxylic acid, *α-truxillic acid*, $C_6H_5CH{-}CHCOOH$ / $C_6H_5CH{-}CHCOOH$, m.p. 275°, forms from cinnamic acid (*q.v.*) by illumination (B. **35**, 2908, 4128), and is found among the subsidiary alkaloids of *cocain* (*q.v.*). By distillation it again decomposes into two molecules of cinnamic acid.

Diphenyl-tetrene-dicarboxylic acid $C_6H_5C{=}CCOOH$ / $C_6H_5C{=}CCOOH$, m.p. 259°, formed by polymerisation of phenyl-propiolic acid, on heating, or with $POCl_3$; easily forms an anhydride or imide (B. **35**, 1407).

Pinic acid $CO_2H.CH\ C(CH_3)_2$ / $CH_2.CHCH_2CO_2H$ and **norpinic acid** $CO_2H.CH.C(CH_3)_2$ / $CH_2.CHCO_2H$ are disintegration products of *pinene* (see Terpenes), in which a tetramethylene ring, the so-called *piceane* ring, is assumed.

C. Pentacarbocyclic Compounds.

The number of known pentacarbocyclic compounds is much greater than that of the tri- and tetracarbocyclic compounds. They are derived partly from cyclo-pentane or pentamethylene, partly from cyclo-pentene. Cyclo-pentadiene is found in the inital products of raw benzene, as obtained from coal-tar. Pentamethylenes, and hexa-

methylenes, have also been obtained from the naphthenes of Caucasian petroleum; and hexamethylenes are partially transformed into the isomeric pentamethylene derivatives by heating alone, or with HI under pressure (cp. A. **324**, 1, etc.). Cyclo-pentane and its progeny have been obtained, not only by the methods of ring synthesis specified on pp. 4, 5, and 6, but also from hexacarbocyclic ring ortho-diketones by intramolecular atomic displacement (see Chloro-diketo-pentamethylene): This last reaction will be met with again in dealing with the disintegration of aromatic substances. In the same manner some remarkable pentamethylene derivatives have been obtained from hexa-oxy-benzol: croconic acid and leuconic acid, which are dealt with below under hexa-oxy-benzol.

Camphor, which is easily converted into aromatic substances, and which contains a five-membered carbon ring, the so-called "*campho-ceanic* ring," gives in different reactions pentamethylene derivatives, *e.g.* camphorphorone, camphoric acid, campholenic acid, campholytic acid, etc. Camphor and its cyclic transformation products are dealt with in connection with the terpenes among the hydro-aromatic compounds, after the benzol derivatives.

1. HYDROCARBONS. — **Pentamethylene,** *R-pentene, cyclopentane* $CH_2\langle^{CH_2—CH_2}_{CH_2—CH_2}$, b.p. 50°, from pentamethylene iodide by reduction. **Methyl-pentamethylene,** b.p. 70°, contained in the so-called hexa-naphthene from Caucasian petroleum (C. 1898, II. 412, 576); formed synthetically from 1, 5-dibromhexane, also from methyl-cyclopenta-none, as well as tert.-methyl-cyclopentanol (C. 1899, I. 1211; B. **35,** 2686). **1, 2-Methyl-ethyl-cyclopentane,** b.p. 124°. **1, 3-Dimethyl-pentamethylene,** b.p. 93°, from the corresponding ketone, is optically inactive; but from the iodide of the 1, 3-dimethyl-tert.-cyclopentanol by reduction an optically active 1, 3-dimethyl-cyclopentane, b.p. 91°, $[\alpha]_D$ 1·78°, and also from 1, 3-ethyl-methyl-cyclopentanol **1, 3-Methyl-ethyl-cyclopentane,** b.p. 121°, $[\alpha]_D$ 4·34°, is obtained (B. **35,** 2678). **1, 2-Diphenyl-pentamethylene,** m.p. 47°, and **1, 2, 3, 4-Tetraphenyl-pentamethylene** from anhydro-aceton- and anhydrodi-benzyl-ketone-benzile (C. 1901, II. 407, 1310). **Triphenyl-methyl-** and **Triphenyl-dimethyl-pentamethylene** from the corresponding cyclic pina-cones (C. 1903, I. 568).

Dipentamethenyl, *dicyclopentyl* $C_5H_9{\cdot}C_5H_9$, b.p. 190°, from penta-methenyl bromide with Na (C. 1899, II. 367).

Cyclopentene $CH\langle^{CH—CH_2}_{CH_2—CH_2}$, b.p. 45°, from pentamethylene iodide or bromide with potash, or from cyclopentanol with P_2O_5 (C. 1899, II. 367), yields with ozone an ozonide $C_5H_8O_3$, which in water decom-poses, forming glutardialdehyde (B. **41,** 1701). **Perchloro-cyclopentene** C_5Cl_8, m.p. 41°, b.p. 283°, from hexachloro-cyclopentenone with PCl_5 (B. **23,** 2214). **Methyl-cyclopentene** $CH\langle^{CH—CHCH_3}_{CH_2—CH_2}$, b.p. 70°, $[\alpha]_D$ 59·07°, from 3-methyl-cyclopentanol by means of zinc chloride or oxalic acid, also from the iodide with KOH. By oxidation it is split into α-methyl-glutaric acid, which, together with the optical activity, proves the formula assumed (B. **26,** 775; **35,** 2491). Isomeric with the methyl-cyclopentene is the **Methylene-cyclopentane** $CH_2.CH_2\rangle C=CH_2$, $CH_2.CH_2$

b.p. 78°–81°, a liquid of penetrating odour, produced from cyclopenteneacetic acid by rejection of CO_2; *nitroso-chloride*, m.p. 81°. Gives a glycol, m.p. 40°, by oxidation with MnO_4K, and also cyclopentanone (A. **347**, 325). Similarly, **1 - Methyl - 3 - methylene - cyclopentane** $CH_2{=}C{<}\begin{matrix}CH_2\\CH_2.CH_2\end{matrix}{>}CH.CH_3$ has been obtained from methyl-cyclopenteneacetic acid. By oxidation it is split into 1, 3-methyl-cyclopentanone (B. **34**, 3950; C. 1902, I. 1222). Like methyl-cyclopentene, it is optically active. In comparison with the corresponding saturated hydrocarbons, the strong optical activity of the unsaturated hydrocarbons with five-membered rings is very remarkable.

Ethylidene-cyclopentane $\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH_2\end{matrix}{>}C{:}CHCH_3$, b.p. 114°, **Isopropylidene-cyclopentane** $\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH_2\end{matrix}{>}CC{<}\begin{matrix}CH_3\\CH_3\end{matrix}$, b.p. 136°, from cyclopenteneisobutyric acid, with displacement of the double linking. By alcoholic sulphuric acid it is isomerised to Δ^1-isopropyl-cyclopentene (A. **353**, 307).

Cyclopentadiene, *pentol* (cp. B. **22**, 916) $CH_2{<}\begin{matrix}CH{=}CH\\CH{=}CH\end{matrix}$, b.p. 41°, an initial product in obtaining raw benzene from coal-tar, is a colourless liquid, violently attacked by both acids and alkalies. It reduces ammoniacal silver solution. It soon polymerises, at ordinary temperatures, to a bimolecular compound, **Dicyclopentadiene** $(C_5H_6)_2$, b.p.$_{35}$ 88°, which at 170° boils with partial re-formation of cyclopentadiene. It is much more stable than the monomolecular compound, and resembles the terpenes in its behaviour (B. **39**, 1492; C. 1906, II. 1403). On heating under pressure, both the simple and the dimeric cyclopentadiene are transformed into a higher-molecular polymer, which again can be split to simple cyclopentadiene (B. **35**, 4151).

The H atoms of the CH_2 group of cyclopentadiene have reaction capacities similar to those contained in the group $.CO.CH_2.CO$ (see Vol. I.). With K in benzene solution it yields the highly reactive potassium-cyclopentadiene, which absorbs CO_2 with formation of a potassium salt of the bi-cyclopentadiene-carboxylic acid $(C_5H_5.COOH)_2$, m.p. 210°, and dimethyl ester, m.p. 85°. With oxalic ester cyclopentadiene in the presence of sodium ethylate it condenses to cyclopentadiene-oxalic ester $C_5H_5.COCOOC_2H_5$; with N_2O_3 an isonitro-derivative is formed. With aldehydes and ketones, under the influence of Na alcoholate, coloured hydrocarbons are formed, which, referred to the hypothetical simplest representation $\begin{matrix}CH{=}CH\\CH{=}CH\end{matrix}{>}C{=}CH_2$, are termed *fulvenes*: **Dimethyl-fulvene** $C_5H_4:C(CH_3)_2$, b.p. 46°; **Methyl-ethyl-fulvene** $C_5H_4:C(CH_3)C_2H_5$, b.p. 185°, orange-coloured oils; **Diphenyl-fulvene** $C_5H_4:C(C_6H_5)_2$, deep-red prisms, m.p. 82°. Further fulvenes, see A. **348**, 1. Like cyclopentadiene itself, the fulvenes absorb the oxygen of the air, and form peroxides, *e.g.* $[C_5H_4:C(CH_3)_2]O_4$ (B. **33**, 666; **34**, 68, 2933).

Cyclopentadiene unites with the quinones in molecular proportions to form stable compounds, like cyclopentadiene-quinone $C_{11}H_{10}O_2$, greenish-yellow flakes of m.p. 78° (A. **348**, 31). With 1 or 2 molecules of the halogen hydrides and the halogens cyclopentadiene yields addition products like: monochloro-cyclopentene C_5H_7Cl, b.p.$_{40}$ 50°; trichloro-

cyclopentane $C_5H_7Cl_3$, b.p. 196°; tetrachloro-cyclopentane $C_5H_6Cl_4$, b.p.$_{15}$ 94°. Monochloro-cyclopentene gives with anilin anilino-cyclopentene $C_5H_7.NC_5H_{10}$, b.p.$_{23}$ 94°–96° (B. **33**, 3348). By adding 2Br to the conjugate double links of cyclopentadiene (Thiele), two stereo-isomeric 1·4-dibromides are generated $\begin{matrix}CH—CHBr\\CH—CHBr\end{matrix}\!\!>\!CH_2$, a solid one and a liquid one, which, on oxidation, yield two stereo-isomeric $\alpha\alpha_1$-dibromo-glutaric acids (A. **314**, 296). Methyl-ethyl-cyclopentadiene, see below.

1, 2, 4-Triphenyl- and **1, 2, 3, 4-Tetraphenyl-cyclopentadiene**, m.p. 149° and 177°, as well as triphenyl-methyl- and triphenyl-dimethyl-cyclopentadiene, m.p. 163° and 128°, are obtained from the corresponding cyclic pinacones by splitting off $2H_2O$ (C. 1898, II. 924; 1903, I. 568; B. **36**, 933).

2. ALCOHOLS.—**Cyclopentanol** C_5H_9OH, b.p. 139°; chloride, b.p. 115°; bromide, b.p. 137°; iodide, b.p. 164°; amine, b.p. 107° (A. **275**, 322). **3-Methyl-cyclopentanol** $HOCH\!\!<\!\!\begin{matrix}CH_2—CHCH_3\\CH_2—CH_2\end{matrix}$, b.p.$_{12}$ 49°; amine, b.p.$_{12}$ 42° (B. **25**, 3519; **26**, 775). Both alcohols are obtained by the reduction of the corresponding ketones.

2-Methyl-cyclopentanol, b.p. 148°, from methyl-cyclopentenone. 1- or tert.-methyl-cyclopentanol, m.p. 30°, b.p. 136°, from the corresponding amine, b.p. 144°, obtained by reduction from the nitrification product of methyl-pentamethylene; also from cyclopentanone with CH_3MgI, as well as by direct synthesis from δ-aceto-butyl-iodide with Mg (p. 4, and B. **35**, 2684; C. 1899, I. 1212).

1, 3-Dimethyl-tert.-cyclopentanol, b.p.$_{94}$ 89°, from 1-methyl-3-cyclopentanone with CH_3MgI (B. **34**, 3950).

Pentamethylene-glycol $C_5H_8(OH)_2$, m.p. 49°, b.p.$_{12}$ 127°, from the dibromide of the cyclopentene (C. 1899, II. 367). A further number of glycols of the pentamethylene series have been obtained by intramolecular pinacone formation (p. 4) by reduction from the 1, 5-diketones (see C. 1901, II. 406; 1903, I. 588).

Pentamethylene-carbinol $C_5H_9CH_2OH$, b.p. 162°, from cyclopentyl-magnesium chloride and trioxy-methylene. Also by the action of HNO_2 on **pentamethylene-methylamine** $C_5H_9CH_2NH_2$, b.p. 139°–145°, besides the cyclohexanol (*q.v.*) produced by a peculiar ring expansion (A. **353**, 325; B. **41**, 2629).

1-Isopropyl-cyclopentane-1, 6-diol $\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\!\!>\!C(OH)—C(OH)\!\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$, m.p. 62°, b.p.$_{14}$ 108°, produced by action of CH_3MgI upon α-oxy-cyclopentane-carboxylic ester. On heating with dilute SO_4H_2 or oxalic acid, the pinacone undergoes the pinacolin transformation with extraordinary facility, 2, 2-dimethyl-cyclohexanone being formed with displacement of a methylene group and expansion of the ring (A. **376**, 152).

$$\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\!\!>\!C(OH)\,C(OH)\!\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}\longrightarrow CH_2\!\!<\!\!\begin{matrix}CH_2—CO\\CH_2—CH_2\end{matrix}\!\!>\!C\!\!<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}.$$

3. RING-KETONES.—The cyclic ketones obtained from calcium salts and the anhydrides of adipinic acid and the alkyl-adipinic acids by methods 7 and 7*a*, p. 6, formed the starting material for the prepara-

tion of the corresponding alcohols, from which later the saturated, and unsaturated, pentacarbocyclic hydrocarbons were obtained. The oximes of these ketones yield on treatment with concentrated SO_4H_2, δ-lactames by Beckmann's transformation (see Vol. I.).

Adipin-ketone [*cyclopentanone*], *keto-pentamethylene* $CO\langle^{CH_2—CH_2}_{CH_2—CH_2}$, b.p. 130°, is found in the wood acids (B. **31**, 1885), and is also generated from 2-keto-pentamethylene-carboxylic ester by ketone splitting. It smells like peppermint, and yields n-glutaric acid on oxidation. Oxime, m.p. 120° (A. **275**, 312). Heating with acetic anhydride to 180° gives, with partial enolisation, *cyclopentenol* acetate, b.p. 156°–158°. With benzaldehyde, adipin-ketone condenses easily to a mono- or dibenzal compound $C_6H_5CH : (C_5H_6O)$ and $C_6H_5CH : (C_5H_4O) : CHC_6H_5$ (B. **29**, 1601, 1836; **36**, 1499; C. 1908, I. 637). With HNO_2 we get di-iso-nitroso-cyclopentanone $HON : (C_5H_4O) : NOH$, m.p. 215° (C. 1909, II. 1549). By sodium ethylate two and three molecules of the cyclopentanone are condensed, forming cyclopentane-pentanone $(C_5H_8O) : (C_5H_8)$, b.p.$_{12}$ 118°, and cyclodipentane-pentanone $(C_5H_8) : (C_5H_4O) : (C_5H_8)$, m.p. 77°, b.p.$_{12}$ 190° (B. **29**, 2962). **3-Methyl-cyclopentanone** $CO\langle^{CH_2—CHCH_3}_{CH_2—CH_2}$, b.p. 142°, is optically active, [α] 135·9° (B. **35**, 2489), and smells like camphorphorone (*q.v.*), which belongs to the cyclopentenones, but is only dealt with in connection with camphor. The oxime of methyl-cyclopentanone is split up by P_2O_5 to the nitrile of hexylenic acid C_5H_9CN, with β-methyl-pyridine as a by-product (C. 1899, II. 947). Cp. the similar behaviour of other cyclic ketones.

A **2-Methyl-cyclopentanone**, which also boils at 142°–144°, has been obtained from α-methyl-adipinic acid (B. **29**, R. 1115). **2, 5-Dimethyl-cyclopentanone**, b.p. 146°, from $\alpha\alpha_1$-dimethyl-adipinic acid (B. **29**, 403). **2, 3, 3-Trimethyl-cyclopentanone** from α, β, β-trimethyl-adipinic acid is related to camphoric acid (B. **33**, 54). A large number of other homologues of cyclopentanone have been prepared by method *7a*, p. 6, from the anhydrides of the alkylated adipinic acids (C. 1908, II. 776).

1, 3-Dimethyl-4, 5-diphenyl-cyclopentanone $^{C_6H_5.CH—CH(CH_3)}_{C_6H_5.CH—CH(CH_3)}\rangle CO$, m.p. 122°, by reduction of dimethyl-anhydro-acetone-benzile with HI and P. As an intermediate product we obtain **1, 3-Dimethyl-4, 5-diphenyl-Δ^4-cyclopentenone**, m.p. 122° (C. 1905, I. 172).

Methyl-cyclopentenone $CH_3.C\langle^{CO—CH_2}_{CH—CH_2}$, b.p. 157°, in wood oil. Oxime, m.p. 128° (B. **27**, 1538).

Phenyl-cyclopentenone $C_6H_5C\langle^{CH_2—CH_2}_{CH—CO}$, m.p. 84°, from phenacyl-acetone (*q.v.*) with dilute NaOH. Oxime, m.p. 147° (B. **41**, 194).

Diphenyl-cyclopentenolone, *anhydro-acetonebenzile* $^{C_6H_5C=CH}_{C_6H_5C(OH).CH_2}\rangle CO$, m.p. 149°, from benzile (*q.v.*) and acetone. By condensation with other ketones, such as methyl-ethyl-ketone and dibenzyl-ketone, several more such ketone alcohols, of the cyclopentene series, have been formed; from benzile and lævulinic acid (Vol. I.) we obtain similarly a **Diphenyl-cyclopentenolone-acetic acid** or anhydro-benzile-lævulinic acid (C. 1899, II. 1051; 1901, II. 1310; 1903, I. 569). An isomeric

diphenyl-cyclopentenolone $\begin{matrix}C_6H_5CH—CH_2\\ C_6H_5C=C(OH)\end{matrix}\!\!>\!CO$, m.p. 176°, is obtained by the action of concentrated SO_4H_2 upon dibenzal-acetone, which is oxidised by potassium permanganate to benzile, and desyl-acetic acid (*q.v.*). With HI both isomeric compounds are reduced to **1, 2-Diphenyl-cyclopentane** (B. **37,** 1133).

Hexachloro-cyclopentenones $\begin{matrix}CCl_2.CCl_2\\ CCl=CCl\end{matrix}\!\!>\!CO$, m.p. 28°, b.p.$_{80}$ 156°, and $\begin{matrix}CCl.CCl_3\\ CCl\ CCl_2\end{matrix}\!\!>\!CO$, m.p. 92°, b.p.$_{75}$ 148°, by oxidation with CrO_3, from the corresponding α-oxy-acids, obtained from benzene derivatives, like o-amido-phenol and pyro-catechin (B. **24,** 926; **25,** 2697). For the action of NH_3 upon these ketones, see C. 1898, I. 607.

1, 2-Diketo-pentamethylene $\begin{matrix}CO—CH_2\\ CO—CH_2\end{matrix}\!\!>\!CH_2$, m.p. 56°, produced by ketone splitting of the 1, 2-diketo-pentamethylene-3, 5-dicarboxylic ester. The diketone has *acid* qualities. In accordance with the desmotropic formula of a **Cyclopentenolone** $\begin{matrix}CO———CH_2\\ C(OH)=CH\end{matrix}\!\!>\!CH_2$, it forms salts and reacts with acetyl chloride, benzoyl chloride, and phenyl cyanate (B. **35,** 3201).

Chlorine easily acts upon diketo-pentamethylene, with formation of **3-Chloro-1, 2-diketo-pentamethylene**, m.p. 139°. Chlorinated 1, 2-diketo-pentamethylenes are also formed in a manner analogous to the chlorinated cyclopentenones, from benzoyl derivatives, like phenol, and chloranilic acid. From potassium chloranilate with chlorine and water we obtain: $\begin{matrix}CO.CCl_2\\ CO.CHCl\end{matrix}\!\!>\!CO$, m.p. 125° (B. **25,** 848). Starting from resorcin, **Tetrachloro-diketo-R-pentene** $\begin{matrix}CCl—CO\\ CCl—CO\end{matrix}\!\!>\!CCl_2$, m.p. 75°, b.p.$_{27}$ 148°, was obtained (B. **24,** 916; **25,** 2225).

The primary disintegration products of the benzene derivatives serving as basic products in these reactions are often chlorinated ketonic acids. Thus, in the last case, from resorcin the acid $CCl_2.CO.CCl : CClCCl_2$ COOH, perchlor-acetyl-crotonic acid, in which the ring completion to the keto-pentamethylenes is then carried out by heating with concentrated sulphuric acid (B. **26,** 513). In a similar manner it has been found possible to convert the β, δ-dibromo-lævulinic acid $CH_2Br.COCHBr.CH_2.COOH$ by means of fuming sulphuric acid into two: **Dibromo-diketo-R-pentene** $\begin{matrix}CBr—CO\\ \|\\ CH—CO\end{matrix}\!\!>\!CHBr$, m.p. 99°, and $\begin{matrix}CH—CO\\ \|\\ CH—CO\end{matrix}\!\!>\!CBr_2$, m.p. 137° (A. **294,** 183).

Methyl-triketo-pentamethylene $CO\!\!<\!\begin{matrix}CH(CH_3)—CO\\ CH_2———CO\end{matrix}$, m.p. 118°, from oxalic ester, and methyl-ethyl-ketone, by method 4*b* (p. 4) (B. **39,** 1336).

By analogy, we have from dibenzyl-ketone:

Diphenyl-triketo-pentamethylene, *oxalyl-dibenzyl-ketone* $CO\!\!<\!\begin{matrix}CH(C_6H_5)—CO\\ CH(C_6H_5)—CO\end{matrix}$, m.p. 139°. On heating, it transposes itself into isoxalyl-dibenzyl-ketone, the lactone of an acyclic acid (B. **27,** 1353; A. **284,** 245).

Pentaketo-pentamethylene is the leuconic acid (*q.v.*) produced by oxidation of croconic acid (*q.v.*). Both compounds are dealt with among the oxy-benzo-quinones in connection with rhodizonic acid.

4. ALDEHYDES AND EXTRA-CYCLIC KETONES.—**Cyclopentane-aldehyde** C_5H_9CHO, an oil with a penetrating odour, resembling valeraldehyde, has been obtained by the action of dilute SO_4H_2 on methylene-cyclopentane-glycol (*q.v.*). **Semicarbazone,** m.p. 123°.

Δ^1-Cyclopentenaldehyde $\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}\!\!>\!C.CHO$, an unstable liquid, smelling like benzaldehyde, formed easily by condensation of the dialdehyde of adipinic acid (Vol. I.). Also from the nitroso-chloride of methylene-cyclopentane by rejection of HCl and splitting of the initially formed oxime with dilute acids.

1-Methyl-2-acetyl-pentamethylene $C_5H_8(CH_3)(COCH_3)$, b.p. 170°, from its carboxylic acid.

Acetyl-Δ^1-cyclopentene $\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}\!\!>\!C.COCH_3$, b.p. 173°–174°, smells distinctly of benzaldehyde. Its oxime, m.p. 91°, is generated by HCl rejection from the nitroso-chloride of ethylidene-cyclopentane.

1-Methyl-2-acetyl-Δ^1-cyclopentene $\begin{matrix}CH_2—C(CH_3)\\CH_2—CH_2\end{matrix}\!\!>\!C.COCH_3$, b.p. 191°. Oxime, m.p. 85°, generated from the ϵ-diketonane by Na ethylate. Oxidised with MnO_4K it yields γ-acetyl-butyric acid. The intermediate formation of a 1,6-diketone is also, probably, a step in the formation of :

Pentamethyl - acetyl - cyclopentene $\begin{matrix}(CH_3)_2C—CH_2\\(CH_3)_2C—C(COCH_3)\end{matrix}\!\!>\!CCH_3$, b.p. 210°–230°, by reduction of the mesityl oxide (Vol. I.; C. 1897, II. 579). Concerning similar ring completions of 1,6-diketones to cyclopentene derivatives, see C. 1899, I. 21; 1909, I. 119).

1-Acetyl-cyclopentanone $\begin{matrix}CH_2—CO\\CH_2—CH_2\end{matrix}\!\!>\!CHCOCH_3$, b.p.$_8$ 75°, by method 4*c*, p. 5, from ϵ-keto-œnanthylic acid. By heating with alcoholic Na ethylate the ring is easily split again (C. 1909, II. 119).

By attaching cyclopentanone to benzal-aceto-phenone, by means of alcoholic caustic soda we obtain the diketone $\begin{matrix}CH_2—CH_2\\CH_2—CO\end{matrix}\!\!>\!CH.CH\!<\!\begin{matrix}C_6H_5\\CH_2COC_6H_5\end{matrix}$ (B. **35**, 1445).

5. CARBOXYLIC ACIDS.—**Cyclopentane-carboxylic acid**, b.p. 214°, smells of sweat; **2-Methyl-cyclopentane-carboxylic acid**, b.p. 219°; **2,5-Dimethyl-cyclopentane-carboxylic acid**, three stereo-isomeric forms: m.p. 75°–77°, m.p. 26°–30°, and m.p. 49°–50° :

$\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\!\!>\!CHCOOH$ $\begin{matrix}CH_2.CH(CH_3)\\CH_2.CH_2\end{matrix}\!\!>\!CHCOOH$ $\begin{matrix}CH_2.CH(CH_3)\\CH_2.CH(CH_3)\end{matrix}\!\!>\!CHCOOH.$

These acids have been obtained from the cyclic malonic esters :

$\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\!\!>\!C(COOR)_2$ $\begin{matrix}CH_2.CH(CH_3)\\CH_2.CH_2\end{matrix}\!\!>\!C(COOR)_2$ $\begin{matrix}CH_2.CH(CH_3)\\CH_2.CH(CH_3)\end{matrix}\!\!>\!C(COOR)_2$

obtained from the corresponding alkylene dibromides by method 5 (p. 5) (B. **26**, 2246; **27**, 1228; **34**, 2565).

Cyclopentane-carboxylic acid has been prepared from the chloro-

cyclopentane with Mg and CO_2, and from the corresponding α-oxy-acid. The 2-methyl-cyclopentane-carboxylic acid has been obtained from the corresponding α-acetyl-carboxylic acid.

3-Methyl-cyclopentane-carboxylic acid, b.p.$_{15}$ 116°, $[\alpha]_D$ −5·89°, from the iodide of 3-methyl-cyclopentanol with Mg and CO_2 (B. **35,** 2690). Isomeric with this is cyclopentane-acetic acid $C_5H_9.CH_2COOH$, by disintegration of the condensation product of iodo-cyclopentane with Na-malonic ester (B. **29,** 1907).

Cyclopentane-1, 2-dicarboxylic acid is known in two modifications. The cis-form forms an anhydride, and is generated by heating the cyclopentane-1, 2-tetracarboxylic acid obtained by method 6 (p. 5), or from trimethylene bromide with sodium-malonic ester (B. **18,** 3246; C. 1901, II. 1264).

1, 3-Cyclopentane-tetracarboxylic acid, produced in a similar manner, yields, on heating, **Cis-cyclopentane-1, 3-dicarboxylic acid,** m.p. 121° (anhydride, m.p. 161°), which on heating with HCl is partly transposed into the trans-acid, m.p. 88° (C. 1898, II. 770).

Cyclopentane-1, 2, 4-tricarboxylic acid $C_5H_7(COOH)_3$ is obtained by the splitting of 1, 2, 4-cyclopentane-hexacarboxylic ester, which is formed by method 6 (p. 5), by the action of Br upon pentane-1, 3, 5-hexacarboxylic ester (C. 1900, I. 802).

Cyclopentene-carboxylic acid $C_5H_7.COOH$, m.p. 120°, from the corresponding aldehyde with Ag_2O (C. 1898, II. 761).

Cyclopentene-1, 2-dicarboxylic acid $CH_2\langle\begin{matrix}CH_2—CCOOH\\CH_2—CCOOH\end{matrix}$, m.p. 178°, from $\alpha\alpha_1$-dibromo-pimelinic acid by the action of Na alcoholate (see also p. 5). Also from 1, 2-dibromo-cyclopentane-1, 2-dicarboxylic acid, obtained by bromination of cyclopentane-dicarboxylic acid, by treatment with alcohol, and KI. The acid easily adds 2Br; by melting with potash it is disintegrated to adipinic acid (B. **28,** 655).

Bis-cyclopentadiene-carboxylic acid was mentioned above in connection with cyclopentadiene.

Cyclopentane-acetic acid $C_5H_9CH_2COOH$, b.p. 226°–230°, has been obtained by transposition of cyclopentanol-acetic ester with HBr and reduction of the compound produced. Amide, m.p. 145° (A. **353,** 304).

Several α; β-unsaturated acids are obtained by rejection of water from the oxy-acids dealt with below.

Cyclopentene-acetic acid $(C_5H_8):CHCOOH$, m.p. 52°, b.p.$_{18}$ 128°–130°; **Methyl-cyclopentene-acetic acid** $(CH_3C_5H_7):CHCOOH$, b.p.$_{11}$ 128°; **Cyclopentene-propionic acid** $(C_5H_8):C\langle\begin{matrix}CH_3\\COOH\end{matrix}$, m.p. 108°.

On dry distillation these acids expel CO_2 and pass into cyclopentene-hydrocarbons with semicyclic double linking; see Methylene-cyclopentane (A. **365,** 273; C. 1902, I. 1222). By nuclear synthesis from lævulinic ester with Na alcoholate a **Methyl-cyclopentadiene-carboxyl-propionic acid** $CH_2\langle\begin{matrix}C(CH_3)=CH\\C(COOH):CCH_2CH_2COOH\end{matrix}$ (?) has been obtained, which at 218° gives off CO_2, and melts, forming at first methyl-cyclopentadiene-propionic acid $C_5H_4(CH_3)(CH_2CH_2COOH)$, m.p. 65°, and then methyl-ethyl-cyclopentadiene $C_5H_4(CH_3)(CH_2CH_3)$, b.p. 135°. These substances resemble cyclopentadiene in their behaviour (B. **36,** 944).

Camphoric acid, 1-methyl-2-dimethyl-cyclopentane-1, 3-dicarboxylic acid, is dealt with under camphor (*q.v.*).

6. ALCOHOL-CARBOXYLIC ACIDS.—**α-Oxy-cyclopentane-carboxylic acid** $\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CO_2H\\OH\end{matrix}$, m.p. 103°, from cyclopentanone CyH and HCl (A. **275,** 333), yields by reduction pentamethylene-carboxylic acid.

1-Methyl-α-amido-cyclopentane-carboxylic acid $CH_3.C_5H_8(NH_2)COOH$, m.p. 299° (B. **39,** 1728). **Hexachloro-α-oxy-cyclopentene-carboxylic acid** $\begin{matrix}CCl_2—CCl_2\\CCl=CCl\end{matrix}\!>\!C\!<\!\begin{matrix}CO_2H\\OH\end{matrix}$, generated from chlorinated cyclohexene-1, 2-diketone with $NaCO_3$ or sodium acetate. On heating it passes into an isomeric acid (B. **23,** 824). Both acids, boiled with water, yield *perchloro-indone* (*q.v.*) (A. **272,** 243). **Trichloro-cyclopentene-dioxy-carboxylic acid** $\begin{matrix}C(OH)—CCl_2\\CCl——CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CO_2H\\OH\end{matrix}$, by the action of chlorine on alkaline phenol solution (B. **22,** 2827).

1, 1-Cyclopentanol acid ester $\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}OH\\CH_2COOC_2H_5\end{matrix}$, b.p.$_{11}$ 105°–107°, by condensation of cyclopentanone and bromacetic ester by means of zinc. In the same manner we obtain **3-Methyl-1, 1-cyclopentanol-acetic ester** $C_5H_7(OH)(CH_2COOC_2H_5)$, b.p.$_{11}$ 90°–92°; **1, 1-Cyclopentanol-propionic ester** $C_5H_8(OH)CH(CH_3)COOC_2H_5$; **1, 1-Cyclopentanol-isobutyric ester** $C_5H_8(OH)C(CH_3)_2COOC_2H_5$, b.p.$_{11}$ 108°–113°.

7. KETONE-CARBOXYLIC ACIDS.—**2-Keto-pentamethylene-carboxylic ester** $\begin{matrix}CH_2.CH(CO_2R)\\CH_2.CH_2\end{matrix}\!>\!CO$, from adipinic ester by method *4a*, p. 4; this ester may be regarded as a carbocyclic derivative of aceto-acetic ester, and shows its typical reactions (Vol. I.). With Na alcoholate and methyl iodide it yields **1-Methyl-2-keto-pentamethylene-carboxylic ester,** b.p.$_{22}$ 108°, and by ketone splitting, keto-pentamethylene. By acid splitting, adipinic acid is regenerated. With amyl nitrite and Na ethylate, α-oximido-adipinic ester is produced.

4-Methyl-2-keto-pentamethylene-carboxylic ester from β-methyl-adipinic ester (A. **317,** 27, etc.; C. 1908, I. 1169).

Keto-pentamethylene-3, 4-dicarboxylic acid $CO\!<\!\begin{matrix}CH_2.CHCO_2H\\CH_2.CHCO_2H\end{matrix}$, b.p. 189°, by condensation of aconitic ester and Na-malonic ester, and subsequent disintegration (B. **26,** 373).

Keto-pentamethylene-2, 3-dicarboxylic ester $CH_2\!<\!\begin{matrix}CO—CHCOOC_2H_5\\CH_2—CHCOOC_2H_5\end{matrix}$, b.p.$_{18}$ 166°, obtained from butane-1, 2, 4-tricarboxylic ester by method *4a* (p. 4). On saponification it expels CO_2, and passes into:

Keto-pentamethylene-3-carboxylic acid, $CH_2\!<\!\begin{matrix}CO—CH_2\\CH_2—CH.COOH\end{matrix}$, m.p. 65° (C. 1908, II. 1781).

A **Phenyl-keto-pentamethylene-dicarboxylic acid** has been prepared by condensation of 2-phenyl-1, 3, 4-butane-tricarboxylic ester (A. **315,** 219).

A **Trimethyl-keto-pentamethylene-dicarboxylic ester,** obtained from dimethyl-butane-tricarboxylic ester by condensation with Na and methyl iodide, possibly contains an atomic group similar to that of camphoric acid (C. 1900, II. 332).

1-Imino-2-cyano-cyclopentane $\begin{matrix}CH_2—CH(CN)\\CH_2—CH_2\end{matrix}\!\!>\!C=NH$, m.p. 147°, produced by intramolecular condensation of adipinic dinitrile with Na ethylate. Similarly, **2-Imino-3-cyano-cyclopentane-1-carboxylic ester** $\begin{matrix}CH_2—CH(CN)\\CH_2—CH(CO_2R)\end{matrix}\!\!>\!C=NH$, m.p. 119·5°, is obtained by the action of sodium cyanacetic ester upon 1, 1-cyano-trimethylene-carboxylic ester where an intermediate production of $\alpha\alpha_1$-di-cyanadipinic ester must be assumed. On treatment with acids we obtain in succession: **3-Cyano-2-keto-pentamethylene-carboxylic ester,** b.p.$_{18}$ 172°–174°, **Cyano-cyclopentanone** $\begin{matrix}CH_2—CH(CN)\\CH_2—CH_2\end{matrix}\!\!>\!CO$, b.p. 229°, and, finally, cyclopentanone (C. 1909, II. 14).

Several 1, 2-diketo-pentamethylene-carboxylic acids have been obtained by method 4*b* (p. 4), by condensation of oxalic ester with esters of the glutaric acid series, and similar acids, *e.g.* **1, 2-Diketo-pentamethylene-3, 5-dicarboxylic ester** $\begin{matrix}CO.CH(CO_2R)\\CO.CH(CO_2R)\end{matrix}\!\!>\!CH_2$ (B. **35,** 3206), and the corresponding methylated and phenylated ester in the 4-position. Some interest attaches to the ester of **4, 4-Dimethyl-1, 2-diketo-pentamethylene-3, 5-dicarboxylic acid** $\begin{matrix}CO.CH(CO_2H)\\CO.CH(CO_2H)\end{matrix}\!\!>\!C(CH_3)_2$, which has been made to pass in succession into *apocamphoric acid*, and dimethyl-pentamethylene-dicarboxylic acid, by replacement of the keto-oxygen atoms by hydrogen (A. **368,** 126).

By similar syntheses we obtain from oxalic and tricarbullylic ester: **1, 2-Diketo-pentamethylene-3, 4, 5-tricarboxylic ester**; from oxalic acid acetone-dicarboxylic ester: **1, 2, 4-Triketo-pentamethylene-3, 5-dicarboxylic ester** (C. 1897, II. 892; B. **29,** R. 1117).

2-Methyl-1-acetyl-pentamethylene-carboxylic acid $CH_2.CH(CH_3)\!\!>\!C\!<\!\begin{matrix}COCH_3\\COOR\end{matrix}$, obtained by method 5 (p. 5), is an extracyclic ketone-carboxylic ester (B. **21,** 742).

A special group is formed by some substances, in which a five-membered ring includes a three-membered ring, the so-called bicyclopentanes. By condensation of $\alpha\alpha_1$-dibromo-β-dimethyl-glutaric ester with Na-malonic ester a *dimethyl-keto-bicyclopentane-tricarboxylic ester* is formed, through the intermediary of a **Dimethyl-trimethylene-dicarbo-malonic ester**:

$$(CH_3)_2C\!<\!\begin{matrix}COOR\\CHBr\\CHBr\\COOR\end{matrix}\longrightarrow(CH_3)_2C\!<\!\begin{matrix}COOR\\C—CH(COOR)_2\\CH\\COOR\end{matrix}\longrightarrow(CH_3)_2C\!<\!\begin{matrix}COOR\\C—CH.COOR\\C—CO\\COOR\end{matrix}$$

The tricarboxylic ester is changed by successive rejection of 2COOR into **Dimethyl-keto-bicyclopentane-di-and-monocarboxylic acid** $(CH_3)_2C\!<\!\begin{matrix}C(COOH).CH(COOH)\\CH———CO\end{matrix}$ and $(CH_3)_2C\!<\!\begin{matrix}C(COOH).CH_2\\CH———CO\end{matrix}$. In the latter acid the trimethylene ring is broken up with formation of **2-Dimethyl-4-keto-pentamethylene-carboxylic acid** (B. **35,** 2126; B. **42,** 2770).

D. Heptacarbocyclic Compounds.

These substances have lately acquired additional importance through their relations with alkaloids and terpenes, as well as the

so-called isophenyl-acetic acid. The frequently easy transformation of heptacarbocyclic compounds into benzene derivatives is worthy of note. Synthetically, most of the suberane derivatives have been obtained by starting from suberone (cp. A. **275**, 356).

Suberane, *heptamethylene*, *cycloheptane* $\begin{matrix}CH_2.CH_2.CH_2\\CH_2.CH_2.CH_2\end{matrix}\!\!>\!CH_2$, b.p. 117°, generated by reduction of suberyl bromide or iodide. By bromine and Al bromide suberane is converted into penta-bromo-toluol (*q.v.*); by heating with HI, into methyl-cyclohexane and hexa-hydro-toluol (B. **27**, R. 47).

Ethyl-suberane $C_7H_{13}.C_2H_5$, b.p. 163°, from zinc ethyl and suberyl bromide. Two molecules of suberyl bromide and sodium yield *di-suberyl* $C_7H_{13}.C_7H_{13}$, b.p. 291° (A. **327**, 70).

Suberene, *cycloheptene* $\begin{matrix}CH.CH_2.CH_2\\CH.CH_2.CH_2\end{matrix}\!\!>\!CH_2$, b.p. 114°, obtained from suberyl iodide with alcoholic potash. Also from suberylamine by treatment with suberyl-trimethyl-ammonium hydroxide, and distillation of the latter (A. **317**, 218). Combines with Br to form a dibromide.

Δ^1-Methyl-suberene $\begin{matrix}CH_2.CH_2.CH\\CH_2.CH_2.CH_2\end{matrix}\!\!>\!CCH_3$, b.p. 138°, from methyl-suberol on heating with potassium bisulphate. On oxidation with MnO_4K it yields ϵ-acetyl-capronic acid. Nitroso-chloride, m.p. 106° (A. **345**, 139). Isomeric with this hydrocarbon is:

Methylene-cycloheptane $\begin{matrix}CH_2.CH_2.CH_2\\CH_2.CH_2.CH_2\end{matrix}\!\!>\!C=CH_2$, b.p. 139°, obtained by distillation of suberene-acetic acid. Nitroso-chloride, m.p. 81°; MnO_4K oxidises to glycol $(C_6H_{12}):C(OH)CH_2OH$, m.p. 50°, which, on further action, passes into oxy-suberane-carboxylic acid and into suberone (A. **345**, 146).

Cycloheptadiene, *heptamethylene-terpene*, *hydro-tropilidene* $\begin{matrix}CH:CH.CH_2\\CH:CH.CH_2\end{matrix}\!\!>\!CH_2$, b.p. 121°, by distillation of the quaternary ammonium bases generated by the complete methylation of the various amino-cycloheptenes (see below), produced partly by synthesis and partly by disintegration of tropin. Combines with Br to a 1, 4-dibromide, which, on heating with quinolin, rejects 2HB and becomes:

Cycloheptatriene, *tropilidene* $\begin{matrix}CH.CH:CH\\CH.CH:CH\end{matrix}\!\!>\!CH_2$, b.p. 116° (A. **317**, 204); the dibromide of the latter passes into benzyl bromide on heating to 100° with HBr (B. **31**, 1544).

Suberyl-alcohol, *cycloheptanol*, $C_7H_{13}.OH$, b.p. 184°, is formed besides suberyl-pinacone by reduction of suberone with Na and alcohol; by strong reduction with HI, suberyl-alcohol is converted into hexahydro-toluol (B. **30**, 1216). Chloride, b.p. 174°; bromide, b.p.$_{40}$ 101°; iodide, D_{15} 1·572. **Suberylamine**, $C_7H_{13}.NH_2$, b.p. 169°, by reduction of suberone oxime, or from suberane-carboxyl amide with KOBr (B. **26**, R. 813; A. **317**, 219).

Methyl-suberol $(C_6H_{12}):C(OH)CH_3$, b.p. 183°–185°, from suberone with $Mg(CH_3)I$.

Cycloheptenol-ethyl ether, $C_7H_{11}.OC_2H_5$, b.p. 174°, from suberene dibromide with alcoholic potash.

Suberyl-methylamine $(C_7H_{13}).CH_2NH_2$, b.p. 193°–195°, from the

amide of suberane-acetic acid with Br and alkali. Nitrous acid gives suberyl-carbinol, and azealol (A. **358**, 327).

Δ^2-Amino-cycloheptene $\begin{matrix}CH_2.CH_2.CH_2\\CH_2.CH:CH\end{matrix}\!\!>\!CH.NH_2$, b.p. 166°, from Δ^2-cycloheptene-carboxylic amide with KOBr, yields on methylation **Δ^2-dimethyl-amino-cycloheptene** $C_7H_{11}.N(CH_3)_2$, b.p. 188°. This is also produced from suberene dibromide with dimethylamine, and shows positive isomerism with the two methyl-tropanes interpreted as Δ^3- and Δ^4-dimethyl-amino-cycloheptene, produced by disintegration of the alkaloid tropin (A. **317**, 204 *seq.*).

Suberone [*cycloheptanone*] $\begin{matrix}CH_2—CH_2—CH_2\\CH_2—CH_2—CH_2\end{matrix}\!\!>\!CO$, b.p. 180°, smells of peppermint. From distillation of Ca suberinate. Passes on oxidation into pimelinic acid. Condenses like adipin-ketone with benzaldehyde into a dibenzal form, m.p. 108° (B. **29**, 1600). Suberone oxime $C_7H_{12}(NOH)$, m.p. 23°, b.p. 230°, is transposed by concentrated H_2SO_4 into ζ-heptolactame (see Vol. I.) Semicarbazone, m.p. 164°.

Δ^1-Methyl-suberenone $\begin{matrix}CH_2.CH_2.CO\\CH_2.CH_2.CH\end{matrix}\!\!>\!C.CH_3$, b.p. 200°–205°. Its oxime has been obtained from the nitroso-chloride of Δ^1-methyl-suberene by rejection of HCl (A. **345**, 145).

Suberane-aldehyde $\begin{matrix}CH_2.CH_2.CH_2\\CH_2.CH_2.CH_2\end{matrix}\!\!>\!CH—CHO$, an oil smelling strongly of benzaldehyde, from the glycol of methylene-cycloheptane by the action of dilute H_2SO_4 (A. **345**, 149).

Δ^1-Suberene-aldehyde $\begin{matrix}CH_2.CH_2.CH\\CH_2.CH_2.CH_2\end{matrix}\!\!>\!C.CHO$ also smells strongly of benzaldehyde. It has been obtained from the nitroso-chloride of methylene-suberane by withdrawal of HCl, and splitting of the oxime thus generated with acids. Silver oxide oxidises it to suberane-carboxylic acid.

Suberane-carboxylic acid, *cycloheptane-carboxylic acid*, $C_7H_{13}CO_2H$, $b.p._{15}$ 139°. Amide, m.p. 195°, has been obtained synthetically from **Suberane-1, 1-dicarboxylic acid,** the ester of which is formed to a slight extent from hexamethylene bromide and Na-malonic ester (B. **27**, R. 735). Suberane-carboxylic acid is also obtained from suberyl bromide with Mg and CO_2 in ether, and by reduction from the various cycloheptene, heptadiene, and heptatriene carboxylic acids. With Br and P it yields **α-Bromo-suberane-carboxylic acid,** m.p. 93°, which, by rejection of HBr, gives:

Δ^1-Cycloheptene-carboxylic acid $C_7H_{11}COOH$, m.p. 52°. Amide, m.p. 126°. This acid is also obtained, by heating with caustic alkali, from the isomeric **Δ^2-Cycloheptene-carboxylic acid,** m.p. 19°; amide, m.p. 158°. Both acids have also been obtained, together with some other isomers, by the reduction of cycloheptatriene-carboxylic acids or their dihydrobromides (A. **317**, 234).

Cycloheptadiene-carboxylic acid $C_7H_9.COOH$, m.p. 78°, identical with hydro-tropilidene-carboxylic acid, a disintegration product of hydro-ecgonidin (*q.v.*).

Cycloheptatriene-carboxylic acids, *tropilidene-carboxylic acids, isophenyl-acetic acids*, $C_7H_7.COOH$: α, m.p. 71° (amide 129°); β, m.p. 56° (amide 98°); γ, liquid (amide 90°); δ, m.p. 32° (amide 125°). The isomerism of these acids is governed by the various positions of the

three double linkages. With HBr they form mono-, di-, and even trihydrobromides, but on energetic treatment with HBr they are transposed into the dihydrobromide of *p-toluylic acid*. They have been obtained: (1) by disintegration of the alkaloid ecgonin, which therefore, like the related tropin, contains a seven-member carbon ring (B. **31**, 2498); (2) by transposition of the pseudo-phenyl-acetic acid or *norcaradiene-carboxylic acid* (C. 1900, I. 811). The latter, generated from benzene and diazo-acetic ester (Vol. I.) by rejection of N, has the formula $\begin{matrix}CH=CH-CH\\CH=CH-CH\end{matrix}\!\!>\!CHCOOH$, and represents the combination of a six-member ring with a trimethylene ring, and therefore a condensed nucleus such as is dealt with below. Similar combinations are probably also contained in the terpene-ketones *carvone* (*q.v.*) and *eucarvone* (*q.v.*), of which the latter passes by reduction into dihydro-eucarvone, which should be regarded as methyl-gem-dimethyl-cycloheptenone $CH_3CH\begin{matrix}CO-CH_2-C(CH_3)_2\\CH_2-CH=CH\end{matrix}$ (B. **31**, 2068).

1-Oxy-suberane-carboxylic acid, *suberyl-glycolic acid*, $C_7H_{12}(OH)CO_2H+\frac{1}{2}H_2O$, melts anhydrously at 79°. From suberone with HCy and HCl; also from α-bromo-suberane-carboxylic acid with baryta water (B. **31**, 2505). With PbO_2 it may be oxidised again completely to suberone (B. **31**, 2507). With concentrated HCl or PCl_5 it passes into chloro-suberanic acid, m.p. 43° (A. **211**, 117; B. **31**, 2004).

α-Amido-suberane-carboxylic acid $C_7H_{12}(NH_2)COOH$, m.p. (anhydrous) 306°–307° (B. **39**, 1730).

1-Oxy-suberane-acetic acid, *cycloheptanol-acetic acid* $C_6H_{12}>C\begin{matrix}OH\\CH_2COOH\end{matrix}$; the esters of this acid (methyl, b.p.$_{12}$ 141°–145°; ethyl, b.p.$_{11}$ 134°) are obtained from suberone and brom-acetic esters with Zn or Mg. On heating with potassium bisulphate, the esters split off H_2O and pass into esters of **Suberylene-acetic acid** $C_6H_{12}>C=CHCOOH$, b.p.$_{17}$ 159°, which, on distillation at atmospheric pressure, decomposes into CO_2 and methylene-cycloheptane $C_6H_{12}>C=CH_2$ (H. **314**, 156; B. **35**, 2143). By transposition with halogen hydrides, oxy-suberane-acetic acid yields bromo- and iodo-suberane-acetic acid, m.p. 69° and 81°, which by reduction pass into **Suberane-acetic acid** $(C_7H_{13})CH_2COOH$, b.p.$_{19}$ 165°. Amide, m.p. 148° (A. **358**, 301).

E. Octocarbocyclic Compounds.

The doubly unsaturated hydrocarbons of cyclo-octane have lately attracted particular interest on account of their relations to rubber. Pseudo-pelletierin, the alkaloid closely related to tropin and tropinone, also contains the eight-member carbon ring. It forms the basis for the majority of the compounds here to be described.

Cyclo-octane $\begin{matrix}CH_2-CH_2-CH_2-CH_2\\CH_2-CH_2-CH_2-CH_2\end{matrix}$, m.p. 11·5°, b.p. 146°–148°, D_4 0·849, has been obtained by reduction of β-cyclo-octadiene with Ni and H.

$\Delta^{1,5}$-Cyclo-octadiene $\begin{matrix}CH_2-CH=CH-CH_2\\CH_2-CH=CH-CH_2\end{matrix}$, b.p.$_{16}$ 39°, D_4 0·884, generated together with small quantities of an isomeric, bicyclic

hydrocarbon during distillation of the quaternary ammonium base obtained by thorough methylation of N-methyl-granatanin, a reduction product of pseudo-pelletierin (*q.v.*) (cp. the analogous preparation of cycloheptadiene from tropane). The cyclo-octadiene is a mobile oil of penetrating odour, the vapour of which is poisonous. It polymerises with extraordinary facility even in the cold, and explosively on heating. This produces a dicyclo-octadiene $(C_8H_{12})_2$, m.p. 114°, and a polycyclo-octadiene $(C_8H_{12})_x$, an amorphous mass with a m.p. above 300°. Ozone transforms the cyclo-octadiene into a di-ozonide $C_8H_{12}O_6$, which, with water, decomposes with formation of succinic dialdehyde. With HBr it combines to form a dihydrobromide $C_8H_{14}Br_2$, b.p.$_{12}$ 150°, from which, by the action of caustic potash or quinolin, a **β-Cyclo-octadiene,** b.p. 143°, is obtained, which is isomeric with the original compound. It has an agreeable odour and shows no tendency to polymerisation (B. **40,** 957).

According to Harries, Para rubber is a polymerisation product of **1, 5-Dimethyl-$\Delta^{1.5}$-cyclo-octadiene** $\left[\begin{matrix}CH_3.C & \!\!\!\

II.—HEXACARBOCYCLIC COMPOUNDS

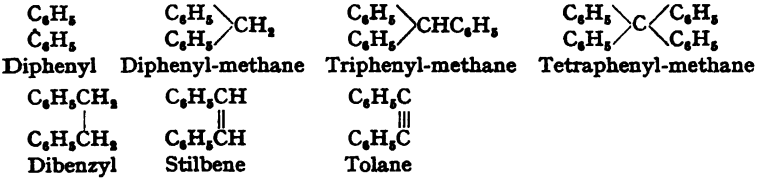
THE chemistry of hexacarbocyclic compounds is incomparably greater and more richly developed than the chemistry of the ring systems dealt with in the preceding chapter. Hexacarbocyclic compounds may be divided into three classes:

A. **Mononuclear aromatic substances, or benzene derivatives.**

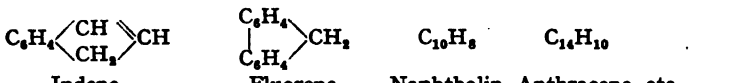
B. **Mononuclear hydro-aromatic substances.** This class contains the terpene group and the camphor group.

C. **Polynuclear aromatic substances.** The fundamental hydrocarbons of this group contain (*a*) several benzene nuclei connected direct or by aliphatic hydrocarbon residues; or (*b*) two or more nuclei are so combined with one another that two carbon atoms are common to each (*twin nuclei, condensed nuclei*).

(*a*)



(*b*)



With each of these hydrocarbons numerous derivatives of all kinds may be associated, thus forming an unlimited field. Many of these bodies, especially naphthalin and its derivatives, give rise to hydro-compounds. These are, however, not dealt with as a separate fourth class, but always in connection with the unhydrogenated derivatives of the hydrocarbons in question.

A. Mononuclear Aromatic Substances or Benzene Derivatives.

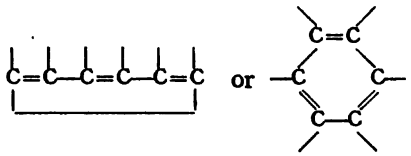
By the name "aromatic" compounds we designate substances which are mostly obtained from aromatic oils and resins, and which differ in general from the fatty bodies or methane derivatives by various peculiarities, especially a greater content of carbon and a well-marked "aromatic" odour. Our theoretical conceptions concerning the constitution of these compounds are mainly derived from the benzene theory formulated in 1865 by Kekulé. It may be summarised in the following theses (cp. Kekulé, *Lehrbuch der org. Chemie*, ii. 493; A. **187**, 129):

1. "All aromatic compounds are derived from a nucleus consisting of six carbon atoms, the simplest combination of which is benzene C_6H_6. They are produced by the replacement of the H atoms by other atoms or groups of atoms (side groups). They all show the specific benzene characteristics, contrasting with the methane derivatives, and should be called '*benzene derivatives.*'"

2. "Benzene has a *symmetrical* constitution. Each carbon atom is joined to an H atom to a carbin group CH. As in the case of the polymethylene derivatives, no differences can be traced between the

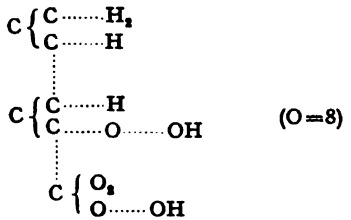
several C or H atoms, and isomerisms of derivatives are therefore only found in the case of two or more side groups."

3. "The structure of the benzene nucleus resembles the methane derivatives in that the six atoms, or CH group, are alternately bound by single and double links, thus making a closed ring-formed chain of six carbon atoms, according to the scheme :



which can also be expressed by a regular hexagon. The fourth valence of the carbon atoms is attached in benzene to an H atom, and in its derivatives to other atomic groups."

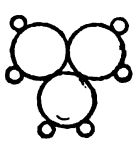
Historical.—The first to invent a structural formula for an aromatic compound was Archibald Scott Couper, who in 1858, in his work on salicylic acid (*C.R.* **46**, 1107), represented it by the formula:

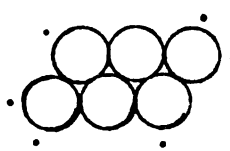


In 1861 J. Loschmidt published a pamphlet called *Chemische Studien* (Wien, Gerold), with new graphic formulæ for 360 substances, among them being 180 aromatic compounds. Loschmidt characterises the aromatic acids as substances with incomplete nuclei, having incompletenesses in eight places. The simplest of these nuclei is C_6^{VI}, for which he brings the six carbon atoms close together:

(Scheme 181 of Loschmidt)

thus obtaining a formula as contained in Couper's salicylic acid formula. He figures the C atoms by means of circles touching where there is single binding, and intersecting where there is plural binding. He prefers, however, a "stratification" of the six C atoms to their

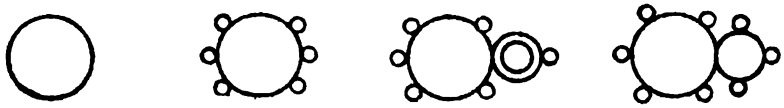

Allyl (Scheme 68).


Benzol nucleus (Scheme 182).

"condensation," and imagines the nucleus as a double allyl nucleus (scheme 182). For allyl, Loschmidt had considered the trimethylene formula (scheme 68). Loschmidt, however, left the question of nuclear constitution in suspense, his constructions being independent

of it. He says: "We assume for the nucleus C_6^{VI} the symbol 184" —a larger circle—" and treat it as if it were a hexavalent element."

Loschmidt then gives graphic formulæ for many benzene derivatives, some of which are given here:



C_6^{VI} (184). C_6H_6 (186). C_6H_5OH (185). $C_6H_5CH_3$ (197).

Of these, 185 represents phenol, and 197 toluol.

Loschmidt had therefore already formed the first thesis of Kekulé's benzene theory. He says nothing about the equivalence of the six benzene H atoms. It was, in fact, excluded on the assumption that the benzene molecule consisted of two stratified allyl rings, since in scheme 182 the free valencies are unequally distributed, as shown by the points of scheme 181. Kekulé, on the other hand, places the structure of the nucleus into the foreground, and derives from it the equivalence of the six H atoms and the explanation of the isomerism of the substitution products.

General Survey of the Benzene Derivatives.

The benzene derivatives can be derived from the replacement of the H atoms of benzene in the same manner as the aliphatic substances are derived from methane. Benzene derivatives with side chains containing carbon may be built up from benzene and brought back to benzene by eliminating the side chains. Benzene derivatives differ from methane derivatives in the stability of the benzene nucleus. Thus oxidation usually stops short at the benzene nucleus, and so does reduction in general, leading finally, as a rule, to cyclohexane derivatives or hexahydro-benzene derivatives, without any splitting of the benzene ring. Reduction therefore connects benzene derivatives with cyclohexane derivatives (p. 2).

Those benzene derivatives which are solid at ordinary temperatures are often distinguished for their ease of crystallisation, and this is a great aid to their experimental investigation.

The H of benzene is easily replaced by the halogens and the groups *nitro* NO_2 and *sulpho* SO_3H:

Chloro-benzene . .	C_6H_5Cl	$C_6H_4Cl_2$	$C_6H_3Cl_3$ . . . . . C_6Cl_6
Nitro-benzene . .	$C_6H_5NO_2$	$C_6H_4(NO_2)_2$	$C_6H_3(NO_2)_3$
Benzol-sulpho-acid .	$C_6H_5SO_3H$	$C_6H_4(SO_3H)_2$	$C_6H_3(SO_3H)_3$

According as to whether one, two, three, or more H atoms of benzene are replaced, we distinguish mono-, di-, tri-, tetra-, penta-, or hexa-derivatives of benzene.

Specially characteristic for the benzene derivatives is the formation of nitro-bodies through the direct action of HNO_3, whereas the aliphatic bodies are generally oxidised or decomposed by it.

Reduction of the nitro-bodies produces the amido-compounds:

Amido-benzene (aniline) $C_6H_5NH_2$ $C_6H_4(NH_2)_2$ $C_6H_3(NH_2)_3$.

As intermediate products of reduction, we have the so-called azo-compounds, while the action of nitrous acid upon amido-compounds produces the diazo-compounds; both classes of bodies are only exceptionally present in the aliphatic series (Vol. I.).

On replacing the H in benzene by hydroxyl we obtain the *phenols*, comparable to the alcohols:

C_6H_5OH	$C_6H_4(OH)_2$	$C_6H_3(OH)_3$
Phenol (carbolic acid)	Dioxy-benzol	Trioxy-benzol.

Like the tertiary alcohols, the phenols contain the group C.OH linked to three C valences, and they cannot therefore form any corresponding aldehydes, ketones, or acids by oxidation.

The benzene nucleus weakens the basic properties of the amido-group and imparts acid properties to phenyl-hydroxyl. It possesses a more negative character than the residues of aliphatic hydrocarbons.

By the entry of monovalent paraffin, olefin, and acetylene residues, the so-called homologous benzene hydrocarbons are derived, both saturated and unsaturated:

C_6H_6	$C_6H_5CH_3$	$C_6H_4(CH_3)_2$	$C_6H_5CH_2.CH_3$	$C_6H_5C_3H_7$, etc.
Benzolene	Methyl-benzol (toluol)	Dimethyl-benzol (xylol)	Ethyl-benzol	Propyl-benzol

$C_6H_5CH=CH_2$	$C_6H_5C\equiv CH$, etc.
Vinyl-benzol (styrol)	Acetylene-benzol.

In these hydrocarbons the benzene nucleus preserves the specific properties of benzene. Its hydrogen is easily replaced by halogens and by the groups NO_2 and SO_3H. But the side chains behave just like the hydrocarbons of the fatty series; its hydrogen can be replaced by halogens, but not (through action of concentrated HNO_3 or H_2SO_4) by the groups NO_2 or SO_3H. According as to whether the halogens (or other groups) enter into the benzene residue or into the side chains, we obtain different isomers:

Chloro-toluol $C_6H_4Cl.CH_3$	Benzyl chloride $C_6H_5.CH_2Cl$
Dichloro-toluol $C_6H_3Cl_2.CH_3$	Chloro-benzyl chloride $C_6H_4Cl.CH_2Cl$

Benzal chloride $C_6H_5CHCl_2$.

The halogen atoms in the benzene residue are firmly held, and usually incapable of a double substitution, while the halogen atoms in the side chains act just as in the methane derivatives.

If in the side chains H is replaced by hydroxyl, we get the true alcohols of the benzene series:

$C_6H_5.CH_2OH$	$C_6H_5.CH_2.CH_2OH$	$C_6H_4\langle^{CH_3}_{CH_2.OH}$
Benzyl-alcohol	Phenyl-ethyl-alcohol	Tolyl-alcohol

the primary ones of which form aldehydes and acids by oxidation:

$C_6H_5.CHO$	$C_6H_5.CH_2.CHO$	$C_6H_4\langle^{CH_3}_{CHO}$
Benzaldehyde	Phenyl-acetaldehyde	Tolyl-aldehyde.

The acids in which COOH is joined to the benzene nucleus may also be produced by direct introduction of carboxyl into the benzene, or by oxidation of the homologues of benzene:

$C_6H_5.CO_2H$	$C_6H_4(CO_2H)_2$	$C_6H_3(CO_2H)_3$
Benzol-carboxylic acid	Benzol-dicarboxylic acid	Benzol-tricarboxylic acid
$C_6H_4\langle^{CH_3}_{CO_2H}$	$C_6H_5.CH_2.CO_2H$	$C_6H_2\langle^{(CH_3)_3}_{CO_2H}$
Toluylic acid	Phenyl-acetic acid	Mesitylenic acid.

In these acids, as well as the alcohols and aldehydes, the H of the benzene residue is also replaceable by halogens and by the groups NO_2, SO_3H, OH, etc.

In the above discussion benzene was regarded as the foundation. The various benzene derivatives with aliphatic side chains were all regarded as benzene substitution products. It is obvious that this view may be reversed. Then the benzene derivatives with a *single* side chain appear, *e.g.* as phenyl substitution products of the aliphatic substances, as exemplified by the following terminology :

$C_6H_5CH_3$	Phenyl-methane	$C_6H_5CH_2CH_2OH$	Phenyl-ethyl-alcohol
$C_6H_5CCl_3$	Phenyl-chloroform	$C_6H_5CH_2CHO$	Phenyl-acetaldehyde
$C_6H_5CH_2OH$	Phenyl-methyl-alcohol	$C_6H_5CH_2COOH$	Phenyl-acetic acid
C_6H_5COOH	Phenyl-formic acid	$C_6H_5CH_2CH_2CO_2H$	Phenyl-propionic acid.

Isomerism of the Benzene Derivatives.

Proof of the equivalence of the six H atoms of Benzene.—If in benzene one H atom is replaced by another atom or atomic group, any compound so obtained is only found in one modification ; there is but one chloro-benzene, one nitro-benzene, *one* amido-benzene, *one* toluol, *one* benzoic acid ; so the compounds

$$C_6H_5Cl \quad C_6H_5.NO_2 \quad C_6H_5.NH_2 \quad C_6H_5CH_3 \quad C_6H_5.CO_2H_2 \text{ etc.}$$

are only known in one modification. The six H atoms of benzene are equivalent, like the four H atoms of methane (Vol. I.). Benzene has a symmetrical *structure.*

Historical.—The proof of the equivalence of the six hydrogen atoms of benzene was given in 1869 simultaneously and independently by W. Körner and A. Ladenburg (B. **2**, 274, 1869 ; **7**, 1684 ; **8**, 1666).

1. Both investigators used the transformation of the three monoxy-benzoic acids into the same phenol, in order to prove the equivalence of the three positions taken by the carboxyl in benzene.

According to Körner, it follows from the reduction of the three monochloro-benzoic acids with Na amalgam to the same benzoic acid.

The equivalence of a fourth H atom follows, according to Ladenburg, from the transformation of phenol into bromo-benzol, and from this into benzoic acid. Ladenburg's proof of the equivalence of four H atoms of benzene may therefore be represented as follows :

	a	b	c	d	e	f	
C_6	(OH)	H	H	H	H	H	→ Phenol
C_6	Br	H	H	H	H	H	↓ Bromo-benzol
C_6	(CO_2H)	H	H	H	H	H	↓ Benzoic acid
C_6	(CO_2H)	OH	H	H	H	H	Ortho-oxy-benzoic acid
C_6	(CO_2H)	H	OH	H	H	H	Meta-oxy-benzoic acid
C_6	(CO_2H)	H	H	OH	H	H	Para-oxy-benzoic acid

Körner deduced the equivalence of the fourth H atom with the three H atoms replaced by carboxyl in the three monoxy- and the

three monochloro-benzoic acids from the following facts :—Para-oxy-benzoic acid corresponds to para-nitraniline (Arppe), which is convertible into either paranitro-chloro- or paranitro-bromo-benzene.

Paranitro-chloro-benzene, by replacement of the nitro-group by Br, gives the same parabromo-chloro-benzene as is obtained on substituting Cl for the nitro-group in paranitro-bromo-benzene. Hence the two H atoms which are replaced in para-nitraniline by the nitro- and amido-group respectively, are equivalent, as are also the H atoms replaced by hydroxyl and carboxyl respectively in para-oxy-benzoic acid.

	a	b	c	d	e	f	
C_6	OH	H	H	CO_2H	H	H	Para-oxy-benzoic acid
C_6	NO_2	H	H	NH_2	H	H	Para-nitraniline

	a	b	c	d	e	f			a	b	c	d	e	f
$\rightarrow C_6$	NO_2	H	H	Cl	H	H	⟶	C_6	Br	H	H	Cl	H	H
$\rightarrow C_6$	NO_2	H	H	Br	H	H	⟶	C_6	Cl	H	H	Br	H	H

This proves the equivalence of four H atoms of benzene.

2. Each hydrogen atom of benzene has two pairs of H atoms arranged symmetrically with respect to it, *i.e.* so that the replacement of either of the two H atoms of a pair by the same atom or the same atomic group leads to the same compound.

Körner proves this symmetry as follows for two H atoms. The volatile nitro-phenol which is convertible into pyrocatechin, and therefore belongs to the same series as salicylic acid, may, by replacing two H atoms by one Br atom and one nitro-group respectively, be converted into the same bromo-nitro-ortho-nitro-phenol as is obtained by introducing two nitro-groups into ortho-bromo-phenol:

	a	b	c	d	e	f		a	b	c	d	e	f
C_6	OH	NO_2	H	H	H	H	⟶ C_6	OH	NO_2	H	NO_2	H	Br
C_6	OH	Br	H	H	H	H	⟶						

b = f.

It is therefore clear that in phenol there are two H atoms symmetrical to hydroxyl, and that it is immaterial which of them is represented by bromine, and which by a nitro-group. But if this symmetry is established for one pair of H atoms, it is also established for the second pair, since the symmetry of the first pair is unthinkable without the symmetry of the second pair. Hence follows the equivalence of all the H atoms of benzene.

The symmetrical arrangement of two H-atom pairs in benzene can also be proved as follows. For one pair, *b* and *f*, this thesis follows from the formation of the same ortho-amido-benzoic acid out of two different nitro-bromo-benzoic acids, obtained by the nitration of meta-bromo-benzoic acid (Hübner and Petermann, A. **149**, 129; **222**, 111; Ladenburg, B. **2**, 140):

	a	b	c	d	e	f	
C	CO_2H	H	Br	H	H	H	Meta-bromo-benzoic acid
C_6	CO_2H	NO_2	Br	H	H	H	v-Meta-bromo-ortho-nitro-benzoic acid*
C_6	CO_2H	H	Br	H	H	NO_2	as-Meta-bromo-ortho-nitro-benzoic acid*
C_6	CO_2H	NH_2	H	H	H	H	Ortho-amido-benzoic acid
C	CO_2H	H	H	H	H	NH_2	Ortho-amido-benzoic acid

Hence ab = af.

* The designations *v* and *as* are dealt with below in connection with the tri-derivatives.

For the second pair the proof is furnished by the formation of the same meta-bromo-toluol from two bromine compounds (Wroblewsky, A. **192**, 213; **234**, 154), in which bromine replaces two different H atoms, which therefore are symmetrical with the H atom replaced by the methyl group of toluol : *ac*=*ae*.

a	b	c	d	e	f
C_6CH_3	H	H	$NH(COCH_3)$	H	H
C_6CH_3	H	Br	$NH(COCH_3)$	H	H
C_6CH_3	H	Br	NH_2	H	H
C_6CH_3	H	Br	H	H	H
C_6CO_2H	H	Br	H	H	H

a	b	c	d	e	f
C_6CH_3	H	Br	$NH(COCH_3)$	NO_2	H
C_6CH_3	H	Br	H	NO_2	H
C_6CH_3	H	H	H	NH_2	H
C_6CH_3	H	H	H	Br	H

By oxidation this bromo-toluol passes into the same meta-bromo-benzoic acid which above served as a basis for the proportion of *v*- and *as*-meta-brom-ortho-nitro-benzoic acid. Hence it follows that bromine in the last proof replaces two H atoms other than those replaced by the amido-group in ortho-amido-benzoic acid, and that in benzene there are not one but two pairs of H atoms in symmetrical position with respect to an H atom. This establishes the equivalence of the six pairs of H atoms. (See also Ladenburg, B. **10**, 1218.)

For the second pair of H atoms the proof of symmetry may be given as follows. The ortho-amido-benzoic acid obtained in two ways (see above) may be converted into the same oxy-benzoic acid, viz. salicylic acid, which on nitrogenation gives two different mononitro-salicylic acids. By heating the ethyl ethers of these two nitro-salicylic acids with ammonia the ethoxyl groups can be replaced by the amido-groups, and, from the nitro-amido-benzoic amides, the free nitro-amido-benzoic acids may be obtained, which with nitrous acid and alcohol are converted into the same nitro-benzoic acid. Since this nitro-benzoic acid, obtained from two different nitro-salicylic acids, yields a (meta) amido-benzoic acid different from the amido-benzoic acid from which the salicylic acid was obtained, and since it yields a (meta) oxy-benzoic acid different from salicylic acid, it follows that there are two further H atoms symmetrically placed with respect to the H atom replaced by the COOH group :

a	b	c	d	e	f		a	b	c	d	e	f
C_6CO_2H	NH_2	H	H	H	H	=	C_6CO_2H	H	H	H	H	NH_2
C_6CO_2H	OH	H	H	H	H	=	C_6CO_2H	H	H	H	H	OH
C_6CO_2H	OH	NO_2	H	H	H		C_6CO_2H	H	H	H	NO_2	OH
C_6CO_2H	NH_2	NO_2	H	H	H		C_6CO_2H	H	H	H	NO_2	NH_2
C_6CO_2H	H	NO_2	H	H	H	=	C_6CO_2H	H	H	H	NO_2	H
C_6CO_2H	H	NH_2	H	H	H	=	C_6CO_2H	H	H	H	NH_2	H
C_6CO_2H	H	OH	H	H	H	=	C_6CO_2H	H	H	H	OH	H

For the third oxy-benzoic acid, para-oxy-benzoic acid, only one position therefore remains, viz. the para position, which in benzene is only possible once.

The equivalence of the six H atoms has lately been proved by Noelting in a very simple manner (B. **37**, 1027).

In amido-benzol or aniline the amido-group is easily replaced by bromine, and the latter by the CH_3 group with the aid of methyl iodide

and sodium. In the toluol thus produced the methyl group therefore takes up the same position as the amido-group does in aniline. From the toluol we obtain by nitrogenation three isomeric nitro-toluols, and from these by reduction three toluidins, which by acetylation, oxidation, and the elimination of the acetyl group can be transformed into three different amido-benzoic acids. These all yield, by rejection of CO_2, an amido-benzol identical with the initial product, which proves the equivalence of four H atoms:

	a	b	c	d	e	f		a	b	c	d	e	f
C_6	NH_2	H	H	H	H	H							
C_6	CH_3	H	H	H	H	H							
C_6	CH_3	NH_2	H	H	H	H	C_6	CO_2H	NH_2	H	H	H	H
C_6	CH_3	H	NH_2	H	H	H	C_6	CO_2H	H	H	NH_2	H	H
C_6	CH_3	H	H	NH_2	H	H	C_6	CO_2H	H	H	NH_2	H	H

a=b=c=d.

The proof of the second thesis (that one H atom has two other H atoms placed symmetrically to it) is based upon one of the nitro-toluols just referred to, in which the CH_3 group takes up position *a*. This, on reduction, yields a toluidin from which, by nitrogenation of its acetyl compound and saponification, four isomeric nitro-toluidins are obtained. By elimination of the amido-group these yield four nitro-toluols. Now, it is found that of these two are identical with each other and two with the initial nitro-toluol, which proves the symmetrical position of two pairs of H atoms:

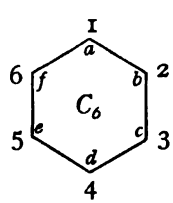
	a	b	c	d	e	f		a	b	c	d	e	f
C_6	CH_3	NO_2	H	H	H	H							
C_6	CH_3	NH_2	H	H	H	H							
C_6	CH_3	NH_2	H	H	H	NO_2							
C_6	CH_3	NH_2	H	H	NO_2	H							
C_6	CH_3	NH_2	NO_2	H	H	H	C_6	CH_3	H	NO_2	H	H	H
C_6	CH_3	NH_2	H	NO_2	H	H	C_6	CH_3	H	H	NO_2	H	H

ab=af ac=ae.

The six H atoms of benzene are therefore equivalent, and, since there are two pairs of symmetrically placed H atoms to each single H atom, a di-substitution product of benzene can only occur in three isomeric modifications.

PRINCIPLES OF LOCATION FOR BENZENE SUBSTITUTION PRODUCTS.

The equivalence of the six H atoms in benzene is expressed by the



hexagon diagram, in which the mutual linking of the C atoms may for the present be disregarded. It is obvious that of each bi-derivative

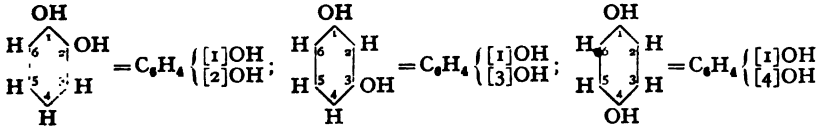
$C_6H_4X_2$ obtained by replacement of two H atoms three modifications are possible and that their isomerism depends upon the relative position of the two new groups entering the benzene scheme. This is called isomerism of position or geometrical isomerism (Vol. I. p. 32). And in fact three modifications are known of most di-derivatives, but not more than three. Thus there are three

$C_6H_4(OH)_2$	$C_6H_4(Br)(NO_2)$	$C_6H_4(NH_2)_2$	$C_6H_4(OH)(NO_2)$
Dioxy-benzols	Bromo-nitro-benzols	Diamido-benzols	Nitro-phenols
$C_6H_4(CO_2H)(OH)$	$C_6H_4(CH_3)_2$	$C_6H_4(CO_2H)(CH_3)$	$C_6H_4(CO_2H)_2$
Oxy-benzoic acids	Dimethyl-benzols	Toluylic acids	Phthalic acids, etc.

The three modifications of each of these compounds can be converted into the corresponding modifications of the others. If, therefore, we have determined the relative positions of the replacing atoms or atomic groups in the three modifications of one of these bodies, it is known for all the others, and they can be converted into the three modifications of the first body by straightforward reactions free from intramolecular atomic displacements. The relative positions of replacing groups have been determined in the case of several di-substitution products, *e.g.* the three dibromo-benzols, the three diamido-benzols, and the three phthalic acids. In this way a basis has been obtained for arranging the other di-substitution products in three series, designated as *ortho-*, *meta-*, and *para*-series respectively.

In the *ortho*-compounds two adjoining H atoms are replaced. If the six H atoms of benzene are indicated by numbers or letters, and any one of them by 1 or *a*, we see that there are two ortho-positions : *a*, *b*=*a*, *f*, or 1, 2=1, 6 ; *b* or 2 and *f* or 6 are symmetrical to *a* or 1. The *meta*-compounds are produced by replacement of the atoms *a*, *c* =*a*, *e*, or 1, 3=1, 5, the positions *c* (3) and *e* (5) being symmetrical to *a* (1). The *para*-compounds are produced by replacing the H atoms *a*, *d* or 1, 4. While, therefore, there are two equivalent places for the *ortho-* and *meta*-positions, viz. 2 and 6, 3 and 5 respectively, the *para*-position has only one location corresponding to 1, viz. 4.

The location of the replacing groups in the di-derivatives is indicated by prefixing *ortho-*, *meta-*, and *para-* to the compounds, abbreviated into *o*, *m*, and *p*, or by prefixing the numbers [1, 2]-, [1, 3]-, [1, 4]- enclosed in square brackets. The formulæ are often represented by writing the benzene ring as a hexagon and attaching the atoms or atomic groups to its corners. Or, again, by introducing the location figures between the benzene residue and the substitution groups :



Pyro-catechin o-Dioxy-benzol [1, 2]-Dioxy-benzol	Resorcin m-Dioxy-benzol [1, 3]-Dioxy-benzol	Hydroquinone p-Dioxy-benzol [1, 4]-Dioxy-benzol.

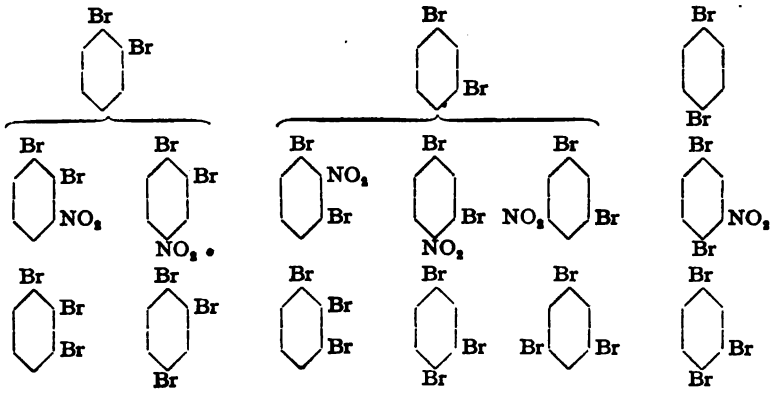
Among the principal representatives of the three isomeric series we may put the following :

	Ortho, [1, 2]	Meta, [1, 3]	Para, [1, 4]
$C_6H_4\langle^{OH}_{CO_2H}$	Salicylic acid	Meta-oxy-benzoic acid	Para-oxy-benzoic acid.
$C_6H_4\langle^{CH_3}_{CH_3}$	Ortho-xylol	Iso-xylol	Para-xylol.
$C_6H_4\langle^{CO_2H}_{CO_2H}$	Phthalic acid	Isophthalic acid	Terephthalic acid.

Location of the Di-derivatives.

The benzene hexagon indicates two chemically identical ortho-derivatives, two chemically identical meta-derivatives, and a single para-derivative, if we neglect the mutual linking of the six C atoms.

The first to indicate a way of experimentally determining the location of the substituents in benzene multiple-substitution products was W. Körner. In 1867 he propounded the opinion that a trioxy-benzol, obtained from any of the three isomeric dioxy-benzols, must necessarily be a 1, 3, 4-trioxy-benzol (*Bull. Acad. Roy. Belg.* 2, **24**, 166). As the transformation of dioxy- into trioxy-benzols was attended with difficulties, Körner replaced the dioxy-benzols by dibromo-benzols, and for these he determined the absolute constitution, in 1874, by conversion into tribromo-benzols (*Gazz. Chim. Ital.* **4**, 305). Körner nitrogenated the three dibromo-benzols. One of them gave two mononitro-dibromo-benzols ; the second, three more ; and the last, one, all different. These six mononitro-dibromo-benzols were then reduced to the corresponding mono-amido-dibromo-benzols, and afterwards transformed into the three tribromo-benzols. Körner showed that in this last transformation the first dibromo-benzol yielded *two* different tribromo-benzols ; the second, *three* different ones ; and the third, only *one* tribromo-benzol. Körner concluded that the first dibromo-benzol had the two Br in the *ortho*-position, the second in the *meta*-position, and the third one in the *para*-position. Thus the absolute position of the bromine atoms in the three tribromo-benzols was determined and the constitution of the six mononitro-benzols was cleared up. The following diagrams illustrate this argument. For the sake of clearness, the H atoms have been omitted.


Br
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NO2
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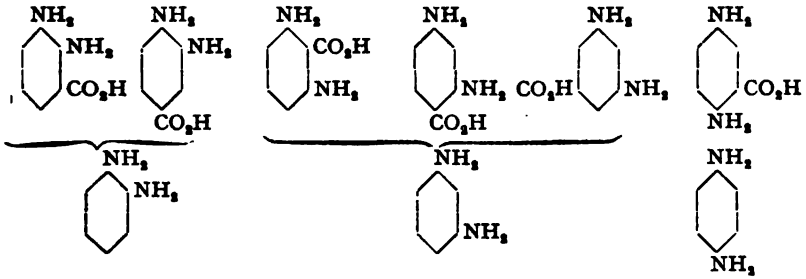
Br

What may be called a reversal of this argument is found in the process experimentally realised by P. Griers (B. **5**, 192; **7**, 1223).

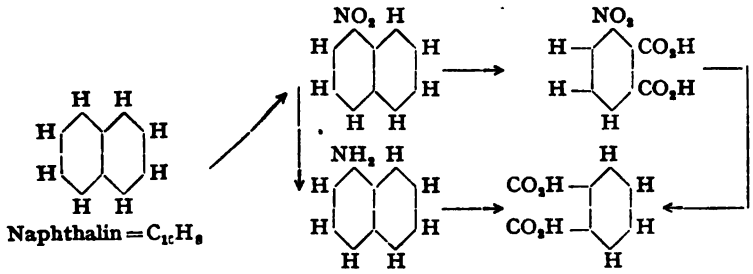
There are six isomeric diamido-benzoic acids, and the diamido-benzol generated by the rejection of CO_2 from two of these acids is the *o*-compound, that which is generated from three of the six acids is the *m*-compound, and that which is generated from the sixth acid is the *p*-compound.



The constitution of benzene derivatives containing side chains is produced by transformation into benzol-carboxylic acids. For the three phthalic acids or benzol-dicarboxylic acids the constitution is determined by the following facts (B. **4**, 101):

The phthalic acid obtained by oxidation of naphthalin is the [1, 2]- or ortho-benzol-dicarboxylic acid. Naphthalin consists of two benzene nuclei having two C atoms in common in the ortho-positions.

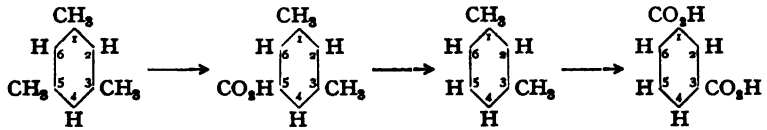
By oxidation of nitro-naphthalin we obtain nitro-o-phthalic acid, which can be converted into phthalic acid; on oxidising the amido-naphthalin obtained by reduction of nitro-naphthalin, we obtain o-phthalic acid, the oxidation destroying, first the one, and then the other, side of the naphthalin molecule. This determines the constitution of both the naphthalin and of phthalic acid as an o-dicarboxylic acid of benzene:



Naphthalin = $C_{10}H_8$ α-Amido-naphthalin Benzol-o-dicarboxylic acid Phthalic acid.

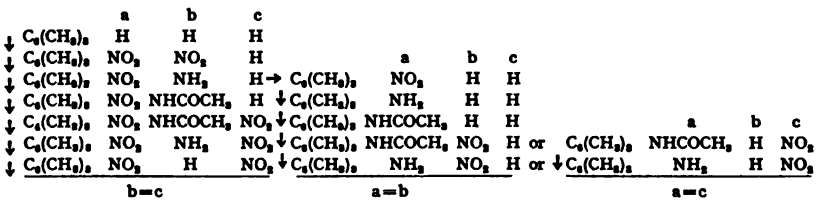
The so-called isophthalic acid is benzol-m-dicarboxylic acid, since it can be obtained by oxidation from isoxylol. Isoxylol is m-dimethyl-benzol, as shown by its formation from mesitylenic

acid, the first oxidation product of mesitylene, or [1, 3, 5]-trimethyl-benzol :



Mesitylene [1, 3, 5]-Trimethyl-benzol — Mesitylenic acid — Isoxylol [1, 3]-Dimethy-benzol — Isophthalic acid Benzol-[1, 3]-di-carboxylic acid.

The proof that mesitylene is really [1, 3, 5]-trimethyl-benzol is due to Ladenburg, who showed that the three unreplaced H atoms of mesitylene are equivalent (A. **179**, 174) :

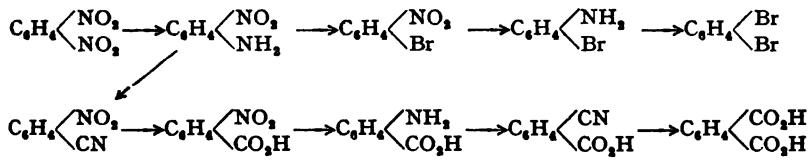


The above scheme clearly illustrates the argument. Mesitylene gives dinitro-mesitylene, of which the NO_2 groups may replace the H atoms *a* and *b*, and then in succession nitro-amido-, nitro-acetamido-, dinitro-acetamido-, dinitro-amido-, and dinitro-mesitylene, identical with the origin. Hence *b* and *c* are equivalent. The nitro-amido-mesitylene, in which we assume the NH_2 group at *b*, yields mono-nitro-, mono-amido-, mono-acetamido-, mono-acetamido-nitro-, and mono-amido-nitro-mesitylene, identical with the first nitro-amido-mesitylene obtained by reduction of dinitro-mesitylene. Hence *a* and *b* or *a* and *c* are equivalent; but, since *b* and *c* are already proved to be equivalent, the equivalence of the three unreplaced H atoms of mesitylene is proved. Mesitylene is symmetrical; therefore its three methyl groups must occupy the positions [1, 3, 5].

For the third benzol-dicarboxylic acid, terephthalic acid, only the 1, 4-position remains, as may be proved as follows :—Terephthalic acid is derived from p-dimethyl-benzol, and this again from p-bromo-toluol (through methyl iodide and Na). Now, p-bromo-toluol yields, by oxidation, p-bromo-benzoic acid; p-bromo-benzoic acid and p-oxy-benzoic acid belong to the same series, for p-oxy-benzoic acid originates in the same p-amido-benzoic acid through the diazo-compound, through which p-bromo-benzoic acid may also be obtained. But of p-oxy-benzoic acid we have already proved that its hydroxyl group represents an H atom symmetrical to no other H atom of benzene.

With the di-derivatives of benzene containing no carbon-bearing radicles as substituents, the three phthalic acids have a genetic relation. The three dinitro-benzols may be converted into nitro-amido-, bromo-nitro-, brom-amido-, and dibromo-benzols on the one hand, and into nitro-cyanic, nitro-carboxylic, amido-carboxylic, cyano-carboxylic,

and phthalic acids on the other hand, by reactions in which no intramolecular atomic displacements are observed (B. **18**, 1492, 1496).



A further proof is furnished by the derivatives of the three isomeric xylols. We have

from Metaxylol,	3 nitroxylols, xylidins, and xylenols
from Orthoxylol,	2 nitroxylols, xylidins, and xylenols
from Paraxylol,	1 nitroxylol.

from which the following positions may be ascertained:

[1, 3] meta- or isoxylol and isophthalic acid
[1, 2] orthoxylol and phthalic acid
[1, 4] paraxylol and terephthalic acid.

(B. **18**, 2687.)

That in the ortho-compounds two neighbouring C atoms of the benzene nucleus hold the side groups, is shown by their capacity for simple reactions, in which a union of the side chains gives rise to carbo- and, especially, hetero-cyclic condensation products (o-phenylene-diamine, o-amido-phenol, o-amido-thiophenol, o-amido-benzaldehyde, o-phthalic acid, o-oxy-cinnamic acid, etc.). There are also crystallographic reasons for supposing that the *meta*-compounds stand between *ortho*- and *para*-compounds (*Zeitschr. f. Kryst.*, 1879, 171; B. **18**, R. 148).

The hexagon scheme of benzene, therefore, not only represents all the isomeric relations of benzene derivatives, but sheds light on their chemical and physical behaviour.

Isomerism of the Benzene Poly-substitution Products.

When three or more H atoms are replaced in benzene, three cases must be distinguished:—The substituents are equal or different. In the first case there are three possible isomers of the tri-derivatives, such as $C_6H_3(CH_3)_3$, with the positions

[1, 2, 3] [1, 2, 4] or [1, 3, 5].

They are termed

adjoining	[1, 2, 3]	or *v* =vicinal
unsymmetrical	[1, 2, 4]	or *as*=asymmetric
symmetrical	[1, 3, 5]	or *s* =symmetric tri-derivatives.

For the tetra-derivatives with four equal groups $C_6H_2X_4$ there are also three possible isomeric structures:

[1, 2, 3, 4] [1, 2, 4, 5] [1, 2, 3, 5].
v s as

With five or six equal groups only one modification is possible; there is but one pentachloro-benzol C_6HCl_5, and only one hexachloro-benzol C_6Cl_6.

If the substituent groups are unequal, the number of possible isomers is much greater; it is easily derived from the hexagon scheme. Thus we have for the formula of dinitro-benzoic acid $C_6H_3(NO_2)_2COOH$ six isomers:

[1, 2, 3] [1, 2, 4] [1, 2, 5] [1, 2, 6] [1, 3, 4] [1, 3, 5],

assigning position 1 to the carboxyl group.

The constitution of the poly-substitution products of benzene is determined by their genetic relations to the di-substitution products of known structure.

Constitution of the Benzene Nucleus.

According to the benzene formula established by Kekulé in 1865, six C atoms are alternately simply and doubly linked into a closed chain. This assumption gives a comprehensive picture of the whole behaviour of the benzene derivatives:

1. It illustrates the synthetic formation of the benzene derivatives, the condensed benzols, naphthalin, phenanthrene, etc.; and is corroborated by all recent syntheses, such as that of α-naphthol from phenyl-isocrotonic acid, etc. (see also B. **24,** 3117).

2. It agrees with the splitting reactions of the benzene nucleus.

3. It explains, in a simple manner, how the ortho-derivatives—on account of the neighbouring position of two side groups—are capable of forming anhydrides and numerous derivatives founded upon an ortho-condensation. The benzene formula also results clearly from the ring formation of quinolin (A. **280,** 1).

4. The existence of three bivalent linkings explains in a simple manner, without new hypotheses, the faculty for forming addition products possessed by the benzene derivatives (p. 45). Such additions do not, indeed, take place with the same ease as in the case of ethylene linkings, in the methane bodies; but aliphatic olefin compounds also show gradual differences in powers of addition (see Allyl alcohol, Vol. I.).

5. Several physical properties also indicate the existence, in benzene bodies, of double linkings similar to those found in ethylene derivatives. Thus, according to Brühl (B. **27,** 1065), the refractivities show that in benzene derivatives there are three ethylene linkings CH=CH (Vol. I.), but in naphthalin five. The specific volumes of the benzene bodies also seem to speak for the existence of three double linkings (Vol. I.).

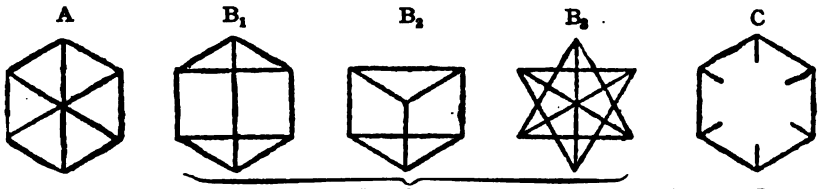
Kekulé's benzene formula does not, however, completely express the symmetry of the benzene nucleus; for it would indicate a difference in the ortho-derivatives [1, 2] and [1, 6], and they would have to give rise to four di-derivatives each—unless we follow Kekulé in assuming oscillations of neighbouring carbon atoms (A. **162,** 86; B. **5,** 463; A. **279,** 195).

Perhaps, during the formation of an ortho-derivative, a displacement of the double linkings occurs when the substituting groups approach two single-linked C atoms, so that what is formed is always

the di-derivative in which the substituent groups are attached to two doubly linked C atoms. This would explain the easier complete oxidation of the o-derivatives, in comparison with the corresponding m- and p-derivatives.

It cannot be denied that the prediction of the existence of two modifications of an ortho-substitution product instead of one constitutes a weakness of Kekulé's benzene formula. It must also be remarked that the many analogies between the ortho- and para-derivatives, in comparison with the meta-derivatives (see Quinone and Quinone derivatives), are not sufficiently expressed by this formula. Still, we give it preference, in comparison with other benzene formulæ, because it gives a consistent view of the connection between aromatic and aliphatic compounds.

Among other benzene schemes we may figure the *diagonal scheme* of Claus (A), the *prismatic scheme* of Ladenburg (B_1, B_2, B_3), and the *centric scheme* of Armstrong and von Baeyer (C).



According to formulæ A and B there are no double linkings in the benzene nucleus. The existence of nine univalent links was supposed to be proved by the specific volume of the benzene compounds, and especially by their heats of combustion ("Theory of Heats of Formation," by J. Thomson, B. **13**, 1808; **19**, 2944). But, according to more recent investigations, the specific volumes rather indicate the existence of three double links in the benzene nucleus, and the conclusions derived from the heats of combustion do not appear to be irrefutable (Brühl, *J. pr. Ch.* 2, **49**, 201).

The prismatic formula of Ladenburg "accounts for all the static conditions of benzene," and illustrates the isomerisms of the benzene derivatives. But it denies all double linkages such as are proved to exist in the partly reduced nuclei of the di- and tetrahydro-addition products; it gives a spatial arrangement, of the four affinities of the carbon atoms, having no analogy among the methane bodies; and, according to its author, "it yields priority to Kekulé's scheme for all processes of formation and decomposition of benzene bodies" (B. **23**, 1010).

Although Claus's diagonal formula is consistent with isomeric relations, and allows of any para- and ortho-additions (B. **20**, 1422; *J. pr. Ch.* 2, **49**, 505), it arranges the four C affinities without analogy, and assumes a peculiar central valency of a new kind.

Baeyer's new centric formula leaves the condition of the fourth C valency indefinite, simply assuming that it exerts a centrally directed pressure. In this way it returns to Kekulé's scheme, which does not profess to explain the linking of the fourth valency (B. **23**, 1272; **24**, 2689; A. **269**, 145; B. **24**, R. 728).

Thiele has lately made a different attempt to explain the required symmetry of the benzene nucleus. He assumes that, in ordinary double linkings, certain "residual valencies" remain, two of which mutually saturate each other when the double linkings adjoin. On assuming such a saturation of all the residual valencies of the three ethylene links, the six C atoms are seen to be linked by six "inactive" double links (A. **308**, 213; **311**, 194).

Some constitutional formulæ for benzene are based upon stereo-chemical considerations, such as Thomson's octahedral formula (B. **19**, 2944), and especially the benzene model of Sachse (B. **21**, 2530; *Z. f. physik. Ch.* **11**, 214; **23**, 2062), as well as that of J. Loschmidt (*Wien. Akad. Ber.* 1890, vol. **99**, ii. p. 20). For later discussions of the various stereo-chemical formulæ, see B. **35**, 526, 703; and C. 1902, II. 350.

Benzene Ring Formations.

The nuclear synthesis reactions of aliphatic substances, in which benzene rings are formed, are important mainly as joining aliphatic and aromatic substances genetically. They will therefore be passed in review, before dealing with the various classes of bodies, in the same succession as that in which the initial bodies were dealt with in the aliphatic series (Vol. I.).

1. CH_4, methane, conducted through an incandescent tube, gives *benzene* and other products.

2. $3CH \equiv CH$, acetylene, polymerises at a red heat to *benzene*.

3*a*. $3CH \equiv C.CH_3$, allylene, polymerises in SO_4H_2 to [1, 3, 5]-*trimethyl-benzol* or *mesitylene*.

3*b*. $3CH_3.C \equiv C.CH_3$, crotonylene, polymerises to *hexamethyl-benzol*.

4. CCl_4, perchloro-methane, and $CCl_2=CCl_2$, perchloro-ethylene, on passing through an incandescent tube, give *perchloro-benzol*; see also *perbromo-benzol*.

5. $3CH \equiv CBr$, monobromo-acetylene, polymerises to [1, 3, 5]-*tribromo-benzol*.

6. $C_6H_{13}I$, hexyl iodide, gives with Cl iodide *hexachloro-benzol*; with bromine, *hexabromo-benzol*.

7*a*. $(CH_3)_2C:CH.CH_2.CH_2C(CH_3):CH.CHO$, geraniol or citral, gives with potassium bisulphate [1, 4]-*isopropyl-toluol* or *cymol*.

7*b*. $CH_3.CH_2CH:C(CH_3)CH:CH.COCH_3$, from methyl-ethyl-acroleïn and acetone, yields *pseudo-cumol*.

7*c*. $(C_3H_7).CH_2CH : C(C_3H_7).CH : CH.CO.CH_3$, from 2 mol. isovaler-aldehyde and 1 mol. acetone, gives *di-isopropyl-toluol* (B. **28**, R. 608).

8*a*. $3CH_3COCH_3$, acetone, gives with SO_4H_2 [1, 3, 5]-*trimethyl-benzol* or *mesitylene*.

8*b*. $3CH_3CO.CH_2CH_3$, methyl-ethyl-ketone, gives [1, 3, 5]-*triethyl-benzol*.

8*c*. $3CH_3CO.CH_2CH_2CH_3$, methyl-n-propyl-ketone, gives [1, 3, 5]-*tri-n-propyl-benzol*.

9. 6CO, carbon monoxide, combines with K on heating to *potassium-hexaoxy-benzol*.

10. $3CH_3CH_2CH_2COCl$, butyryl chloride, is condensed by Al_2Cl_6 into *triethyl-phoroglucin*.

11. $3CH{\equiv}C.CO_2H$, propiolic acid, polymerises in sunlight to [1, 3, 5]-*benzol-tricarboxylic acid* or *trimesinic acid*.

12. $3NO_2CH(CHO)_2$, nitro-malonic aldehyde, gives, on decomposition of its Na salt, sym. *trinitro-benzol*.

13. $NO_2.CH(CHO)_2$, nitro-malonic aldehyde, and CH_3COCH_3, acetone, give *p-nitro-phenol* (B. **28**, 2597 ; C. 1899, II. 609).

14. $3CH_3.CO.CH{=}CHOH$, oxymethylene-acetone or formyl-acetone, condenses easily to [1, 3, 5]-*triacetyl-benzol* $C_6H_3(COCH_3)_3$.

15*a*. $2CH_3CO.CO.CH_3$, diacetyl, condenses with alkalies to *p-xylo-quinone* or [2, 5]-*dimethyl-quinone*.

15*b*. $2CH_3.CO.CO.CH_2CH_3$, acetyl-propionyl, gives *duro-quinone* or *tetramethyl-quinone*.

16. $3CH(OH){=}CH.CO_2C_2H_5$, oxymethylene-acetic ester or formyl-acetic ester, and their dimolecular condensation product, cumalinic acid, condense easily to esters of the [1, 3, 5]-*benzol-tricarboxylic acid* or *trimesinic acid* ; this is also obtained from a mixture of formic and chloracetic acids with zinc (C. 1898, II. 472).

17. $4CH_3COCO_2H$, pyro-traubenic acid, condenses on heating with NaHO with rejection of oxalic acid and water to methyl-dihydro-trimesinic acid, which passes easily into uvitinic acid with rejection of CO_2.

18. $2CHOCH_2CH_2COOH$, β-formyl-propionic acid, gives *terephthalic acid* or *p-benzol-dicarboxylic acid*.

19. $2CH_3CO.CHNa.CO_2C_2H_5$, sodium-acetic ester, and $CHCl_3$, chloroform, combine to *oxy-uvitinic ester* or *oxymethyl-isophthalic ester*, also obtained direct from methenyl-bisacetic ester $CH{<}^{CH(CO_2C_2H_5)COCH_3}_{C(CO_2C_2H_5)COCH_3}$ with Na alcoholate.

20. $2ROCOCH : CH.CH_2COOR$, glutaconic acid ester, unites under the action of sodium ethylate, with rejection of one molecule of alcohol, and acetic ester to form *4-oxy-iso-phthalic acid ester* (B. **37**, 2117).

21. $CH_3C : CH.CO.CH.COCH_3$ (O — CO) dehydracetic acid, yields *orcin* or 3, 5-*dioxy-toluol*.

22. $2CH_3.CO.CH_2.CO.CO_2C_2H_5$, acetone-oxalic ester, is condensed to *oxy-toluylic acid ester*.

23*a*. $CH_3.CH_2CH : C(CH_3).CH : C(COOR)_2$, from methyl-ethyl-acrolein and malonic ester, yields with Na alcoholate *oxy-mesitylenic acid*.

23*b*. $(CH_3)_2 : CH.CH_2.CH_2.C(CH_3) : CH.CH : C(COOR)_2$, citralidene-malonic ester, yields *3-isoamenyl-4-methyl-salicylic acid*.

It is doubtful whether in the formation of *mellithic acid* or *benzol-hexacarboxylic acid* $C_6(CO_2H)_6$ by the oxidation of charcoal or graphite a synthesis occurs ; perhaps this reaction must be regarded as the transformation of a molecule consisting of twelve C atoms.

On again surveying the reactions by which aliphatic bodies are converted into benzene bodies by nuclear synthesis, we find that :

(1) Some saturated compounds, like methane and tetrachloromethane, yield the benzene ring by the action of heat (*pyro-condensation*). Many benzene derivatives, like benzene and the methylbenzols, simple amido- and oxy-benzols, are distinguished for their constancy at high temperatures (see Coal-tar).

(2) During *perchloration* of many aliphatic compounds the occur-

rence of perchloro-benzol was observed. Hexyl iodide is transformed particularly easily into perchloro- and perbromo-benzol.

(3) A large number of aliphatic acetylene compounds containing a triply linked pair of C atoms, yield benzene derivatives by *polymerisation* of three similar molecules. A difficult polymerisation is that of acetylene to benzene. Brom-acetylene is much more easily polymerised. Allylene and crotonylene require sulphuric acid, propiolic acid, and sunlight for aromatic polymerisation.

The other aliphatic compounds above referred to, which may condense themselves to aromatic substances (*aromatic condensation*), contain carbon and oxygen in double linking. Many are ketones, or they contain the oxy-methylene group.

(4) A direct *addition reaction* is exemplified by the manner in which potassium hexa-oxy-benzol is formed from CO and K.

(5) *Hydrolytic condensation* is exemplified by the simple ring formation in the transition of citral or geranial and other high-molecular keto-olefins into cymol, pseudo-cumol, and di-isopropyl-toluol, as well as the condensation of di-hydro-acetic acid to orcin, with liberation of CO_2.

(6) The condensation of acetone, methyl-ethyl- and methyl-n-propyl-ketone to [1, 3, 5]-tri-alkyl-benzols is paralleled by condensation of butyryl chloride to tri-ethyl-phloroglucin, with a triple rejection of HCl; also by the condensation of two molecules β-formyl-propionic acid to terephthalic acid, with rejection of water and hydrogen.

(7) These condensations are related to the condensations of nitro-malonic-acid aldehyde, and the oxy-methylene compounds (12 to 16). Also to

(8) The condensation of the α-diketones to quinones;

(9) Of acetone-oxalic acid to oxy-toluylic acid; and

(10) The condensation of chloroform and sodium-acetic ester to oxy-uvitinic-acid ester, in which methenyl-bis-acetic ester can be assumed as an intermediate product.

(11) The formation of homologous salicylic acids from alkenglidene-malonic esters with Na alcoholate is based upon an intramolecular aceto-acetic ester condensation.

There is also a peculiar condensation of pyro-traubenic acid to methyl-dihydro-trimesinic or uvitinic acid, in which oxalic acid is first split off.

These benzene formations are associated with several reactions leading to hydro-aromatic compounds having a close relation to benzene derivatives. We may mention the following:

1. Sodium-malonic ester condenses to phloroglucin-dicarboxylic ester, formed from acetone-dicarboxylic ester and malonic ester (B. **29,** R. 1117). Sodium-acetonic-dicarboxylic ester condenses to dioxy-phenyl-dicarboxylic ester (B. **31,** 2014; C. 1897, II. 741). All these condensation products are probably derivatives of hexa-hydro-benzol.

Cp. also the condensations of sodium-acetone-dicarboxylic ester with iodine to hydroquinone-tetracarboxylic ester (B. **30,** 2569), with eth-oxy-methylene, aceto-acetic, and eth-oxy-methylene-malonic ester to oxy-trimesinic ester, and resorcin-tricarboxylic ester, respectively (C. 1899, II. 1018, 1020).

2. Succinic acid ester condenses with sodium to succinylo-succinic acid ester.

3. 1, 5-diketo-compounds, which contain, in the terminal place, besides a CO group, a CH_3 or CH_2R group, condense to cyclic aldols, of the hexamethylene series, which easily pass into keto-tetra-hydro-benzene derivatives. Methylene-bis-aceto-acetic ester, α,γ-diacetyl-glutaric ester, thus gives methyl-keto-tetramethylene-dicarboxylic ester. Similarly, with sodium ethylate, the γ-acetyl-butyric ester $CH_3CO.CH_2.CH_2.CH_2.COOC_2H_5$ yields dihydro-resorcin, which can, by a reversed process, pass into γ-acetyl-butyric acid by splitting (cp. benzol ring splitting).

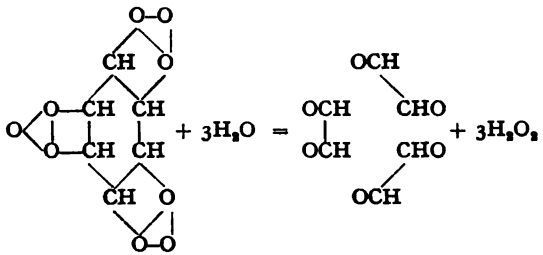
Some other methods of synthesising hydro-aromatic compounds were mentioned on pp. 4 and 5.

Benzene Ring Splittings.

As already mentioned, the benzene derivatives are in general distinguished by the tenacity of the benzene ring. In order to split the benzene ring, suitable benzene derivatives are treated with reagents which, partly or wholly, dissolve the double links of the nucleus. The splitting is therefore always preceded by the formation of hydro-aromatic intermediate products, which, as a rule, could not be retained. Sometimes we obtain split products containing the six nuclear C atoms in the molecule as an open chain, in some cases pentacarbocyclic compounds from hexacarbocyclic α-diketones.

Ring splittings were found most easily practicable in the case of phenols, amido-phenols, quinones, oxy-quinones, and phenol-carboxylic acids.

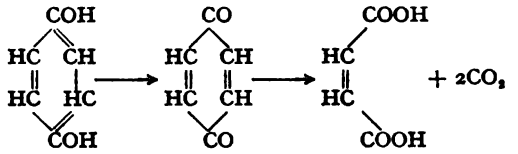
1. **Splitting by feeble oxidation.**—While strong oxidisers convert the benzene nucleus into CO_2, formic acid, and oxalic acid, ozone is capable of producing a straightforward, and extremely clear, splitting of benzene. By addition of three molecules of ozone to the three double links of the benzene nucleus, we get, first, ozobenzol, or benzol-triozonide $C_6H_6O_9$, which is decomposed by water into three molecules of glyoxal (Harries) :



This splitting furnishes one of the strongest supports for Kekulé's benzene formula. The homologous benzene hydrocarbons behave similarly.

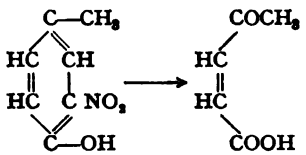
Pyro-catechin or [1, 2]-dioxy-benzol $C_6H_4[1,2](OH)_2$ and proto-catechuic acid or [3, 4]-dioxy-benzoic acid $CO_2H[1]C_6H_3[3,4](OH)_2$ are oxidised to dioxy-tartaric acid (Kekulé).

Hydroquinone or [1, 4]-dioxy-benzol, and the quinone easily generated from this, are split up by silver peroxide into maleïnic acid and CO_2 (R. Kempf) :

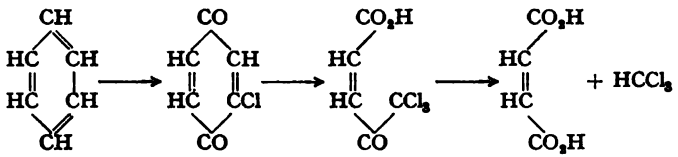


Phenol C_6H_5OH has been transformed by potassium permanganate solution into meso-tartaric acid (Döbner). Probably in this case also quinone is formed in the first instance, and then maleïnic acid, which with MnO_4K passes into meso-tartaric acid (see Vol. I.).

By oxidation of o-nitro-p-cresol with fuming sulphuric acid we obtain β-acetyl-acrylic acid (Schultz and Löw) :



2. **Splitting by simultaneous chlorination and oxidation.**—Benzene treated with potassium chlorate and sulphuric acid passes first into chlorinated quinone and then into trichloro-pheno-malic acid and β-trichlor-acetyl-acrylic acid (see Vol. I.), which with baryta water decomposes into chloroform and maleïc acid (Kekulé and Strecker) :



Benzene — Monochloro-quinone — Trichloro-pheno-malic acid — β-Trichlor-acetyl-acrylic acid — Maleïc acid.

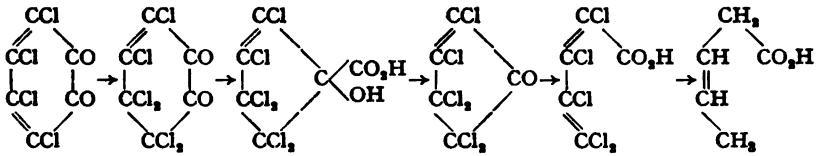
From phenol, salicylic acid, or ortho-oxy-benzoïc acid $COOH[1]C_6H_4[2]OH$, and from gallic acid $COOH[1]C_6H_2[2, 3, 4](OH)_3$, we obtain, by treatment with potassium chromate and HCl, iso-trichloro-glycerinic acid $CCl_3C(OH)_2COOH$ (see Vol. I.).

Picric acid or [1, OH, 2, 4, 6]-trinitro-phenol, treated with bleaching powder, yields chloro-picrin (Vol. I.); with bromine, and lime water, bromo-picrin.

Specially illuminating are the methods of benzene splitting worked out by Zincke. They consist in the formation of chlorinated R-hexene and R-hexylene-ketones, from suitable aromatic compounds, and the splitting of the former.

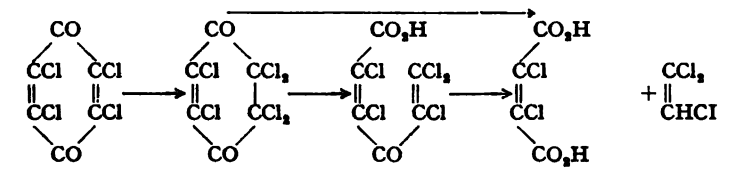
We shall give, in what follows, four examples, the first three of which start from the three dioxy-benzols, and the fourth from [1, 3, 5]-trioxy-benzol, or phloroglucin.

(1) Pyro-catechin or o-dioxy-benzol, treated with chlorine, passes into tetrachlor-ortho-quinone, and then into hexachlor-o-diketo-R-hexene. By merely heating in water the latter is converted into hexachloro-R-pentene-oxy-carboxylic acid, which may be oxidised by means of chromic acid to hexachloro-keto-R-pentene. With caustic soda the hexachloro-R-pentene-ketone splits to form perchloro-vinyl-acrylic acid, which, on reduction, yields ethylidene-propionic acid (B. **27**, 3364) :



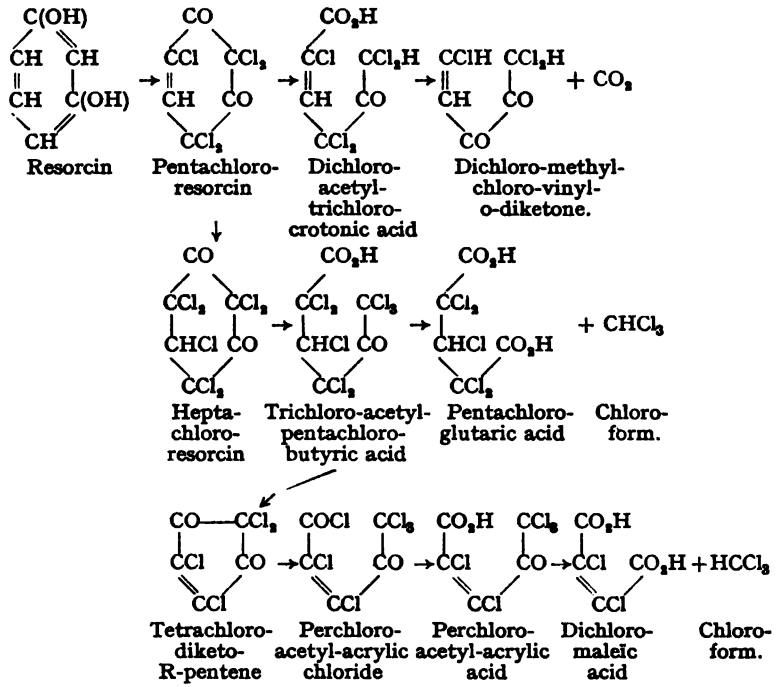
Tetra-chloro-quinone | Hexachlor-o-diketo-R-hexene | Hexachloro-R-pentene-oxy-carboxylic acid | Hexachloro-keto-R-pentene | Perchloro-vinyl-acrylic acid | Ethylidene-propionic acid.

(2) The splitting up of hydroquinone is simpler. By the action of chlorine upon hydroquinone, or quinone, as well as of potassium chlorate and HCl upon phenol, we can easily obtain tetrachloro-para-quinone (chloranile), and from this, by chlorination, hexachloro-para-diketo-R-hexene, which, with alcoholic potash, is broken up to perchlor-acroyl-acrylic acid. The latter, as well as hexachloro-para-diketo-R-hexene itself, are decomposed by aqueous soda into dichloro-maleïc acid and trichlor-ethylene (A. **267**, 1) :

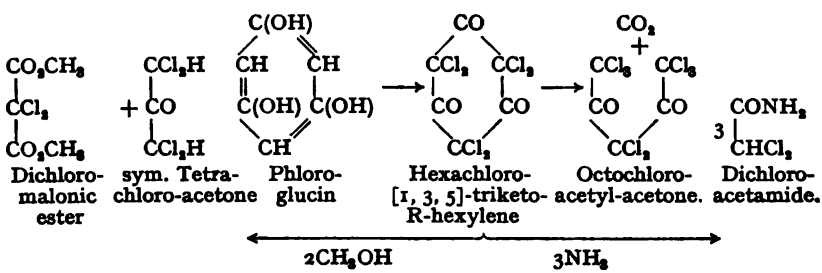


Tetrachloro-p-quinone | Hexachloro-p-diketo-R-hexene | Perchlor-acroyl-acrylic acid | Dichloro-maleïc acid | Trichlor-ethylene.

(3) From resorcin, with chlorine and glacial acetic acid, we obtain pentachloro-resorcin, and, from the latter, heptachloro-resorcin. Both m-diketo-chlorides split up in cold water alone. The pentachloro-compound becomes dichloro-acetyl-trichloro-crotonic acid, and the heptachloro-compound becomes, with chlorine and water, trichloro-acetyl-pentachloro-butyric acid. The dichloro-acetyl-trichloro-crotonic acid, boiled in water, yields dichloro-methyl-chloro-vinyl-o-diketone. The trichloro-acetyl-pentachloro-butyric acid, treated with alkalies, splits into chloroform and pentachloro-glutaric acid, as does trichloro-acetyl-acrylic acid. But on treating it with boiling water it passes into tetrachloro-diketo-R-pentene, which, with chlorine, is transformed into perchloro-acetyl-acrylic chloride. The chloride, with water, yields the acid itself, which again, on treatment with alkalies, decomposes into chloroform and dichloro-maleïc acid :



(4) The behaviour of resorcin closely resembles that of phloroglucin or [1, 3, 5]-trioxy-benzol, as this passes with chlorine into hexachloro-[1, 3, 5]-triketo-R-hexene. The triketone, treated with chlorine and water, decomposes into octochloro-acetone, and, treated with methyl alcohol, into dichloro-malonic-dimethyl ester and sym. tetrachloro-acetone; and, treated with ammonia, into three molecules dichloro-acetamide (B. **23**, 1706):

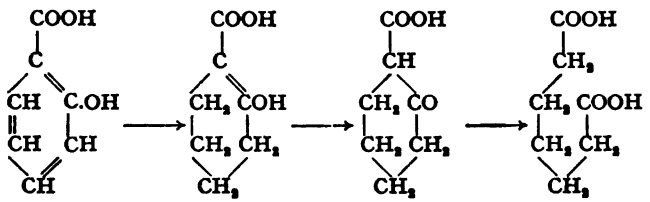


In the four examples the splitting takes place between a CO group and a CCl_2 group of keto-chlorides. These reactions were first developed by Zincke in the naphthalin series, and used for splitting up one of the naphthalin nuclei and for the transformation of naphthalin derivatives into indene derivatives. Later he extended the process to the above-mentioned phenols and other aromatic compounds. In a similar manner Hantzsch carried out the splitting up of phenol with

chlorine in alkaline solution, and its transformation into cyclopentene derivatives (B. **22**, 1238).

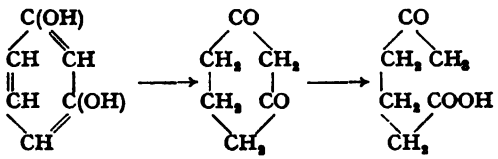
3. **Splitting up by reduction in alkaline solution.** — This splitting occurs in

(1) The o-phenol-carboxylic acids during reduction with Na in amyl alcohol. As intermediate products of the reduction we may assume tetrahydro-acids and their transposition products—hydro-aromatic-o-ketone-carboxylic acids. The latter take up water and change into pimelinic acids; salicylic acid yields almost quantitatively n-pimelinic acid; while o-, m-, and p-cresotinic acids yield the three isomeric methyl-pimelinic acids (Einhorn and Willstätter, B. **28**, R. 744):



This reaction has been transferred with equal success to the naphthalin-o-oxycarboxylic acids (see Naphthalin-ring splittings).

(2) Resorcin gives, on reduction, dihydro-resorcin, which, during oxidation with potassium permanganate, yields n-glutaric acid (Merling, A. **278**, 32); heating for several hours with concentrated baryta solution to 150°–160° splits up dihydro-resorcin to γ-acetyl-butyric acid with addition of H_2O (Vorländer, B. **28**, 2348):



This reaction is reversible.

1. The Single-Nucleus Benzene Carbohydrates.

BENZENE, *phene, benzol*, C_6H_6, m.p. +5·4°, b.p. 80·4°, is the fundamental hydrocarbon of the aromatic substances. It is generated in the dry distillation of coal, and is therefore found in coal-tar, accompanied by a body most closely resembling it in physical properties, viz. thiophene (*q.v.*) C_4H_4S, and numerous other compounds. Pure benzene is formed by heating benzoic acid or benzol-polycarboxylic acids with lime. Synthetically, benzene may be produced from acetylene by heating to high temperatures (Berthelot, 1870).

Benzene is produced from coal-tar by fractionation, and is separated from thiophene (*q.v.*) by repeated shaking up with a little concentrated sulphuric acid, treatment with aluminium chloride, or heating with chlorine sulphide, formaldehyde, or phthalic anhydride (B. **29**, R. 1000,

1152; C. 1902, II. 737; 1909, II. 666). Finally it is purified by squeezing off, after being crystallised in a freezing mixture.

Historical (B. **23,** 1271).—Benzene was discovered by Faraday in 1825, in compressed illuminating gas prepared from oil. It was obtained in 1834 by Mitscherlich by distillation of benzoic acid with quicklime, and was discovered by A. W. Hofmann in 1845 in coal-tar.

Properties.—Benzene is a mobile liquid of an odour resembling ether, D_0 0·899, D_{20} 0·8799. It burns with a luminous flame, mixes with absolute alcohol and ether, and dissolves resins and fats very easily, also many hydrocarbons capable of crystallisation with crystal benzene (see Triphenyl-methane). Sulphur, iodine, and phosphorus are also soluble in benzene.

Behaviour and Transformations.—(1) On conducting benzene through an incandescent tube it is partly changed into diphenyl $C_6H_5.C_6H_5$, and into diphenyl benzols $C_6H_4(C_6H_5)_2$, and decomposes partly into acetylene. (2) On oxidising benzene with Mn peroxide and H_2SO_4 some benzoic acid is formed, obviously due to some diphenyl formed intermediately (A. **221,** 234), also some o-phthalic acid; but benzene is very stable against oxidisers. By silver peroxide in the presence of HNO_3, or by manganic sulphate, it is oxidised to quinone (*q.v.*) (B. **38,** 3963; C. 1908, I. 74). Benzene is split up by treatment with ClO_3K and H_2SO_4, passing into trichloro-pheno-malic acid and β-trichlor-acetyl-acrylic acid. On passing ozone through benzene for some time, a white amorphous mass is obtained, the so-called ozobenzol, a very explosive substance, of the formula $C_6H_6O_9$, decomposed slowly by water with formation of glyoxal (B. **37,** 3431). (3) By heating with HI to 260°–280° benzene is mostly isomerised into methyl-pentamethylene; but benzene and hydrogen combine to hexahydro-benzol, on passing over finely divided nickel at 180°–200° (C. 1901, I. 817). (4) Chlorine and bromine act upon benzene both by addition and by substitution. (5) HNO_3 transforms it into nitro-benzol $C_6H_5NO_2$; and (6) H_2SO_4 into benzol-sulpho-acid $C_6H_5SO_3H$. The last two compounds are prepared industrially on a large scale. With the help of Al_2Cl_6 and halogen alkyls, alkyl residues may be introduced into benzene. (7) With aldehydes, benzene is condensed by H_2SO_4 to higher aromatic hydrocarbons (see Diphenyl-methane and ethane).

Coal-Tar.

Dry distillation of coal also gives rise to many alkyl-benzols, and some higher condensed aromatic bodies like naphthalin $C_{10}H_8$, acenaphthene $C_{12}H_{10}$, fluorene $C_{13}H_{10}$, anthracene and phenanthrene $C_{14}H_{10}$, fluoranthene $C_{15}H_{10}$, pyrene $C_{16}H_{10}$, and chrysene $C_{18}H_{12}$. They are contained in the "coal-tar" obtained in great quantities in gas-works and coke-ovens. Besides illuminating gas and tar, ammonia water is formed, while coke remains in the retorts, forming a fuel richer in carbon than coal itself.

For the rapid and brilliant development of aromatic chemistry it has been of the greatest utility that the fundamental aromatic substances have been made available to chemical investigation, in any

desired quantity, by the industry concerned. For, while the paraffins were unsuitable bases for the building up of aliphatic substances, the aromatic hydrocarbons, with their faculty for the most varied reactions, form not only the systematic but also the practical foundation for the chemistry of aromatic substances. Coal-tar, which contains these hydrocarbons, is the inexhaustible source for preparing numberless aromatic compounds, many of which have been most widely used as dyes, perfumes, and medicines.

Working of Coal-Tar for Aromatic Hydrocarbons.—Coal-tar, which, besides the aromatic hydrocarbons, contains aliphatic bodies, thiophene and its methylated derivatives, phenols, pyridin bases, and other compounds, is first distilled into three or four fractions :

1. **Light oil** (3 to 5 per cent.), lighter than water, boils at 150°.
2. **Middle oil** (8 to 10 per cent.), about the density of water, boils at 150°–210°.
3. **Heavy oil** (8 to 10 per cent.), heavier than water, boils at 210°–270°.
4. **Green oil,** or anthracene oil (16 to 20 per cent.), of a green colour, boils at 270°–400°.
5. **Residue.**—Pitch (about 60 per cent.).

For the benzene compounds only light oil is in question, which is freed from resins, olefins, pyridin bases, etc., by washing with sulphuric acid, and then from phenols by washing with caustic soda. It is then subjected to a careful fractional distillation.

Besides benzene, the following benzene hydrocarbons occur in coal-tar :—Toluol or methyl-benzol, the three isomeric xylols or dimethyl-benzols ; ethyl-benzol, vinyl-benzol or styrol ; the three isomeric trimethyl-benzols ; mesitylene, pseudo-cumol, hemi-mellithol, n-propyl-benzol, the three isomeric toluols, and durol or tetramethyl-benzol. Aromatic hydrocarbons are also found freely in lignite tar, to some extent in wood-tar oil, in slate-tar oil, and in rock-paraffin oil.

The bulk of the benzene and toluol of to-day is obtained from the coke-oven gases, which contain about 42 grammes per cubic metre, by treating the gases with coal-tar fractionings, of higher boiling-points, in spraying towers.

The winning of aromatic bodies by dry distillation should be considered in connection with their formation by *pyrogenic synthesis* or *pyro-condensation*, by conducting aliphatic bodies through incandescent tubes. In dry distillation the retort walls take the place of the tubes (cp. B. **29,** 2691 ; **10,** 853 ; **20,** 660).

Alkyl-Benzols C_nH_{2n-6}.

The first place among the formation processes of alkyl-benzols must be given to the reactions of *nuclear synthesis* (Vol. I.).

1. It has been repeatedly mentioned that various symmetrical trialkyl-benzols are formed by polymerisation of alkyl-acetylenes in the presence of sulphuric acid, just as benzene is produced by the polymerisation of acetylene.

Allylene $3CH_3.C{\equiv}CH \xrightarrow{SO_4H_2} C_6H_3[1,3,5](CH_3)_3$, mesitylene. For the alkyl-acetylenes we may substitute ketones, acetone, ethyl-methyl-ketone, and treat them with sulphuric acid.

2. Much more general is the reaction discovered in 1864 by Fittig: action of Na upon a mixture of brominated benzene hydrocarbons in ether solution, with alkyl-bromides, and iodides (A. **129**, 369; **131**, 303; B. **21**, 3185):

$$C_6H_5Br + CH_3I + 2Na = C_6H_5CH_3 + NaI + NaBr$$

$$C_6H_4Br.C_2H_5 + C_2H_5I + 2Na = C_6H_4\begin{matrix}C_2H_5\\C_2H_5\end{matrix} + NaI + NaBr.$$

This reaction is a very valuable generalisation of Würtz's synthesis of the paraffins, by the action of sodium upon halogen alkyls (Vol. I.). A few drops of acetic ester promote the reaction, which is the smoother, the higher the molecular weight of the alkyl iodide.

3. The synthesis of tetramethyl-methane from acetone chloride, and zinc methyl (Vol. I.), corresponds to the synthesis of iso-propyl-benzol out of benzol chloride and zinc methyl (B. **13**, 45), and of one amyl-benzol out of benzol chloride and zinc ethyl:

$$C_6H_5CHCl_2 + Zn(C_2H_5)_2 = C_6H_5CH(C_2H_5)_2 + ZnCl_2.$$

4. Essentially limited to aromatic compounds, but in these of very general utility, is the so-called aluminium chloride synthesis discovered by Friedel and Crafts in 1877, and consisting in the action of alkyl-haloids upon benzene hydrocarbons in the presence of Al chloride.

In some cases the olefins react in the presence of HCl in a manner similar to the alkyl-haloids (C. 1907, II. 366).

Similar action is shown by zinc chloride, and especially iron chloride (cp. Nencki, B. **32**, 2414). The Al chloride can sometimes be replaced by a mixture of sublimate and Al filings (see B. **35**, 868). Here it is probable that the alkyl-haloids first form organic compounds, which then act upon the hydrocarbons (C. 1900, I. 756; B. **33**, 815). In some cases intermediate products have been preserved. The reaction between benzene, ethyl chloride, and Al chloride seems to traverse the following phases:

$$2C_6H_6 + 3C_2H_5Cl + Al_2Cl_6 = Al_2Cl_6.C_6H_3(C_2H_5)_3.C_6H_6 + 3HCl$$

$$Al_2Cl_6.C_6H_3(C_2H_5)_3.C_6H_6 + 3C_2H_5Cl = Al_2Cl_6[C_6H_3(C_2H_5)_2]_2HCl + 2HCl.$$

This reaction product on heating decomposes into triethyl-benzol, HCl, and the compound $Al_2Cl_6.C_6H_3(C_2H_5)_3$, which under the action of HCl can convert a fresh molecule of benzene into triethyl-benzol, so that one may alkylise a large quantity of benzene with very little Al chloride. Water decomposes the compound $Al_2Cl_6.C_6H_3(C_2H_5)_3$ in $Al(OH)_3$, HCl, and triethyl-benzol (*J. pr. Ch.* 2, **72**, 57). There is no difficulty about replacing all the H atoms of benzene by methyl and ethyl groups (B. **14**, 2624; **16**, 1745). Sometimes CS_2 acts favourably as a diluent (A. **235**, 207; cp. B. **29**, 2884):

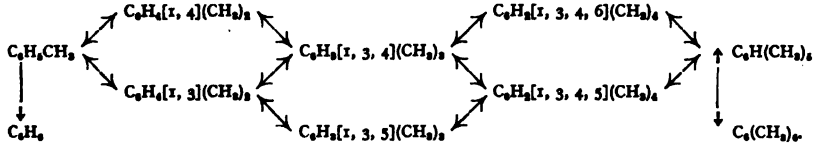
$$CH_3Cl + C_6H_6 \xrightarrow{Al_2Cl_6} HCl + C_6H_5CH_3$$

$$2CH_3Cl + C_6H_6 \xrightarrow{Al_2Cl_6} 2HCl + C_6H_4(CH_3)_2$$

$$6CH_3Cl + C_6H_6 \xrightarrow{Al_2Cl_6} 6HCl + C_6(CH_3)_6.$$

Similar reactions with the benzene hydrocarbons are shown by very different halogen compounds, like chloroform, and the acid chlorides. Ethyl ether also acts, in the presence of Al_2Cl_6, upon benzene hydrocarbons with formation of poly-ethylated benzols (C. 1899, II. 755).

Disintegration reactions.—5. Curiously enough, Al chloride is as suitable for disintegrating the alkyl-benzols as it is for synthesising them. Under suitable conditions it is possible to detach, by means of Al chloride, the side chains from one molecule of a hydrocarbon, and introduce it into another molecule of the same hydrocarbon. In this process, certain positions of the alkyl groups are preferred, both in synthesis and in disintegration, as shown by the following scheme of reactions (Anschütz and Immendorf, B. **18,** 657) :



In the case of butyl- and amyl-benzols an isomerisation of the alkyl radicles is easily effected by Al chloride (C. 1899, I. 776).

If bromine is made to act upon poly-alkalised benzols, in the presence of Al bromide, the longest side chain is split off, with bromination of the resultant products (C. 1899, I. 32).

6. Concentrated sulphuric acid acts similarly, both for synthesis and for disintegration.

7. Dry distillation of a mixture of aromatic acids, with lime or soda-lime, iron filings being added to promote heat-conduction. In this case all carboxyls are split off and the fundamental hydrocarbons are formed :

Benzoic acid	. $C_6H_5CO_2H$	⟶ $CO_2+C_6H_6$	Benzol
Toluylic acid	$CH_3C_6H_4CO_2H$	⟶ $CO_2+C_6H_5CH_3$	Toluol
Phthalic acid	. $C_6H_4(CO_2H)_2$	⟶ $2CO_2+C_6H_6$	Benzol.

8, 9, and 10. *Replacement of inorganic residues in substitution products by hydrogen :*

8. Treatment of diazo-compounds with alcohol and alkaline stannous oxide solution (B. **22,** 587). This reaction is particularly important for solving questions of constitution. The diazo-compounds are obtained from amido-compounds, and the latter from nitro-compounds, produced by the action of HNO_3 upon hydrocarbons.

9. Treatment of sulpho-acids with superheated steam, and sulphuric acid, concentrated HCl, or phosphoric acid, at 180°.

10. Heating of oxygen-containing derivatives, phenols, and ketones, with zinc dust (Baeyer, A. **140,** 295) or HI and phosphorus. It is notable that in this reaction benzo-phenone $C_6H_5.CO.C_6H_5$ is easily reduced, but diphenyl-ether $C_6H_5.O.C_6H_5$ not at all. A special facility is shown in the reduction of the ketones, on passing vapours, with hydrogen, over finely divided nickel at 190°–195° (C. 1905, I. 29).

11. Many alkyl-benzols, like propyl- and isopropyl-benzols, are best produced by reduction of the corresponding olefin-benzols, like

$C_6H_5CH : CHCH_3$ and $C_6H_5C(CH_3) : CH_2$ with Na and alcohol (B. **36,** 621, 1628, 1632; **37,** 1721).

Properties.—The benzene hydrocarbons are mostly volatile liquids, though some polymethyl-benzols (durol, penta- and hexamethyl-benzol, also hexa-ethyl-benzol) are solid at ordinary temperatures. They possess a peculiar, and not unpleasant, odour, and are insoluble in water, though soluble in alcohol and ether. They are themselves good solvents for many organic compounds, which may be precipitated from them by means of petrol ether.

Behaviour and Transformations.—1. With reducing agents, especially when the vapours are conducted with hydrogen over finely divided nickel, the alkyl-benzols and benzene itself pass into hydro-cyclic hydrocarbons. HI produces a transposition of the six-membered into an isomeric five-membered hydrocarbon.

2. Of great importance is the behaviour of alkyl-benzols in oxidation. Dilute nitric acid, chromic acid mixture, potassium permanganate, or ferricyanide convert the side chains of the benzene homologues into COOH groups. The number of COOH groups produced, and their mutual positions, give information concerning the number and position of the alcohol radicles in the oxidised benzene carbohydrates. By careful oxidation, especially with MnO_4K, intermediate products may be obtained, when the side chains are long, the oxidation taking place according to the same rules as in the fatty bodies (cp. aromatic carboxylic acids).

3. Chlorine and bromine, when cold, replace H atoms of the benzene nucleus, and on heating they replace the H atoms of the side chain (see Toluol).

4. Concentrated nitric acid yields nitro-compounds.

5. Concentrated sulphuric acid decomposes alkyl-benzols to sulpho-acids on heating, and, from these, the hydrocarbons can be formed again (by method 9). A process for separating out, and purifying, the benzols has been based upon this.

6. Under the action of ozone the alkyl-benzols, and benzene itself, yield explosive triozonides, which are decomposed by water, with formation of aliphatic aldehydes (A. **343,** 369).

7. With chromyl chloride CrO_2Cl_2 the homologous benzols yield compounds, from which water forms aromatic aldehydes, and ketones (*q.v.*).

8. On heating toluol or xylols with sulphur, stilbene $C_6H_5CH : CHC_6H_5$ is formed, or methylated stilbene, and further transformation products (C. 1903, I. 502).

Isomerism.—Of the first member of the series, *toluol*, the theory only allows of one modification, and this is the only one found. The six H atoms of benzene are equivalent.

Of *xylol* or dimethyl-benzol three isomers are possible, as it is a di-substitution product:

o-Xylol $C_6H_4\{^{[1]CH_3}_{[2]CH_3}$ m-Xylol $C_6H_4\{^{[1]CH_3}_{[3]CH_3}$ p-Xylol $C_6H_4\{^{[1]CH_3}_{[4]CH_3}$.

With these three known xylols ethyl-benzol $C_6H_5C_2H_5$ is isomeric.

Of bodies with the formula C_9H_{12}, eight isomers are possible, and these are all known: (1) three trimethyl-benzols; (2) three ethyl-

methyl-benzols; (3) two propyl-benzols: n-propyl- and isopropyl-benzol.

The isomerisms are therefore determined by the position, number, homology, and isomerism of the alkyls entering the benzene in replacement of hydrogen.

Constitution.—Of the syntheses of the alkyl-benzols, Fittig's reaction (see above) is especially valuable, as regards conclusions respecting constitution, since, as far as we know, no intramolecular atomic displacements occur in it, the alkyls taking the places vacated by the halogen atom. Oxidation also helps in deciding about the number and position of the side chains.

The following table shows the most important alkyl-benzols:

Name.	Formula.	M.p.	B.p.	Density.
Toluol	$C_6H_5CH_3$	..	110·3°	0·8708 (13·1/4°)
Xylols, Dimethyl-benzols	$C_6H_4(CH_3)_2$			
o-Xylol		−28°	142°	0·8932 (0°)
m-Xylol, **Isoxylol**		−54°	139°	0·8812 (0°)
p-Xylol		+15°	138°	0·8801 (0°)
Ethyl-benzol	$C_6H_5CH_2CH_3$	..	136°	0·8832 (0°)
Trimethyl-benzols	$C_6H_3(CH_3)_3$			
[1,2,3]=Hemimellithol		..	175°	..
[1,2,4]=**Pseudo-cumol**		..	170°	..
[1,3,5]=**Mesitylene**		..	164·5°	0·8694 (9·8/4°)
Methyl-ethyl-benzols	$C_6H_4(CH_3)(C_2H_5)$			
o- or [1,2]-		..	159°	0·8731 (16°)
m- or [1,3]-		..	159°	0·8690 (20°)
p- or [1,4]-		..	162°	0·8652 (21°)
n-Propyl-benzol	$C_6H_5CH_2CH_2CH_3$	..	158·5°	0·8810 (0°)
Isopropyl-benzol, **Cumol**	$C_6H_5CH(CH_3)_2$	..	153°	0·8798 (0°)
Tetramethyl-benzol	$C_6H_2(CH_3)_4$			
[1,2,3,4]=Prehnitol		− 4°	204°	..
[1,2,3,5]=Isodurol		..	196°	0·8961 (0/4°)
[1,2,4,5]=Durol		79°	190°	..
Methyl-isopropyl-benzols	$C_6H_4(CH_3)[CH(CH_3)_2]$			
[1,2]-		..	175°	0·8723 (0°)
[1,3]-		..	175°	0·8582 (18°)
[1,4]=**Cymol**		..	175°	0·865
Pentamethyl-benzol	$C_6H(CH_3)_5$	53°	230°	..
Hexamethyl-benzol	$C_6(CH_3)_6$	164°	264°	..
Penta-ethyl-benzol	$C_6H(C_2H_5)_5$	..	277°	0·8985 (19°)
Hexa-ethyl-benzol	$C_6(C_2H_5)_6$	129°	298°	..

From this table it is seen that the position isomers of the same formula, *e.g.* the three xylols, have closely adjoining melting-points. In the dimethyl-benzols the o-compound boils at the highest temperature. Then come the meta- and finally the para-compound; but the p-compound has the highest melting-point. Of the tetramethyl-benzols, durol is solid at ordinary temperatures, also the pentamethyl-, hexamethyl-, and hexa-ethyl-benzols.

The entry of a methyl group produces in the methyl-benzols an elevation of the boiling-point by about 24° to 30°: cp. toluol, xylols, tri-, tetra-, penta-, and hexamethyl-benzols. Entry of CH_2 into a side chain raises the boiling-point by about 24°: cp. toluol, ethyl-benzol, and n-propyl-benzol.

TOLUOL $C_6H_5CH_3$, so called because it is obtained from the dry distillation of tolu balsam, is found in coal-tar in company with thiotolene or methyl-thiophene (*q.v.*), and is very valuable industrially. It is formed according to the general methods :

(1) From bromo-benzol, methyl iodide, and sodium ;
(2) From benzene, methyl chloride, and Al chloride ;
(3) From the polymethyl-benzols and Al chloride ;
(4) From the three toluylic acids, and the methyl-polycarboxylic acids, by distillation with lime, etc.

On reduction, toluol passes into *hexahydro-toluol* ; by oxidation with dilute HNO_3, or chromic acid, into benzoic acid ; with chromyl chloride, CrO_2Cl_2, and water, or MnO_2, Cl_2O_3, and sulphuric acid, into benzaldehyde. On nitrogenation it gives o- and p-nitro-toluol ; on sulphurising it yields much p-toluol-sulpho-acid, besides a little o-acid.

Chlorine has a remarkable action upon toluol. At boiling-point only the hydrogen of the *side chain* is replaced, and we get :

Benzyl chloride $C_6H_5CH_2Cl$
Benzal chloride $C_6H_5CHCl_2$
Benzo-trichloride $C_6H_5CCl_3$.

In the cold, on the other hand, o- and p-chloro-toluol are generated, $C_6H_4Cl.CH_3$. In the presence of iodine and $SbCl_5$ chlorine only enters the nucleus, even at boiling-point (Beilstein and Geitner, A. **139,** 311). But a little PCl_5 facilitates entry into the side chain (A. **272,** 150). The same effect is produced by sunlight.

Hydrocarbons C_8H_{10}.—Ethyl-benzol is isomeric with the three dimethyl-benzols. Of the three xylols occurring in coal-tar, iso- or m-xylol is most abundant and technically important.

During oxidation with dilute HNO_3, o- and p-xylol are oxidised to o-and p-toluylic acid, and the latter to o-and p-phthalic acid respectively. Metaxylol is attacked with greater difficulty. Potassium permanganate also oxidises the three xylols to the corresponding toluylic acids, and finally to phthalic acids. H_2SO_4 dissolves o- and m-xylol to xylolsulphc-acids (B. **10,** 1013 ; **14,** 2625). On distilling raw xylol with steam, p-xylol passes over first.

o-Xylol is also formed from o-bromo-toluol, CH_3I and sodium. Oxidised by MnO_4K it passes into phthalic acid. Chromic acid burns it to CO_2 and H_2O, like many o-derivatives.

m-Xylol or **iso-xylol.**—The production of m-xylol from mesitylenic acid, by heating with lime, is theoretically important. This reaction genetically connects m-xylol with mesitylene, in which the [1, 3, 5]-position of the three methyl groups can be established. This proves the m-position for the toluylic and phthalic acids generated by oxidation of m-xylol.

$$C_6H_3\begin{cases}[1]CH_3\\[3]CH_3\\[5]CH_3\end{cases} \rightarrow C_6H_3\begin{cases}[1]CO_2H\\[3]CH_3\\[5]CH_3\end{cases} \rightarrow C_6H_4\begin{cases}[1]CH_3\\[3]CH_3\end{cases} \rightarrow C_6H_4\begin{cases}[1]CO_2H\\[3]CH_3\end{cases} \rightarrow C_6H_4\begin{cases}[1]CO_2H\\[3]CO_2H\end{cases}$$

Mesitylene — Mesitylenic acid — Isoxylol — m-Toluylic acid — Isophthalic acid

p-Xylol, by distillation of camphor with $ZnCl_2$, also from p-bromotoluol and p-dibromo-benzol, CH_3I and Na (B. **10,** 1355). On oxidation

with dilute HNO_3 it gives first p-toluylic acid, then terephthalic acid, and with CrO_3 terephthalic acid at once. In fuming sulphuric acid it decomposes, forming a well-crystallising sulpho-acid.

Ethyl-benzol $C_6H_5CH_2CH_3$ also occurs in coal-tar (B. **24,** 1955). Produced from bromo-benzol, ethyl bromide, and sodium; or benzol, ethyl bromide. and Al chloride (B. **22,** 2662); also by reduction of styrol $C_6H_5CH=CH_2$. Dilute HNO_3 and chromic acid oxidise it to benzoic acid. CrO_2Cl_2 produces phenyl-acetaldehyde $C_6H_5.CH_2.CHO$.

Hydrocarbons C_9H_{12}—The isomerism of the eight compounds of this formula has already been pointed out above. For physical constants see table.

Mesitylene, *symmetrical trimethyl-benzol,* occurs in coal-tar, and in certain naphtha fractionals (C. 1901, I. 1002), and is prepared from acetone (Kane, 1837) or allylene with concentrated sulphuric acid (cp. B. **29,** 958, 2884). The proof of its symmetrical structure is of fundamental importance for the location of the benzene substitution products. With dilute HNO_3, mesitylene passes into mesitylenic and mesidinic acids, or into uvitinic and trimesinic acids:

$$C_6H_3\begin{cases}[1]CH_3\\[3]CH_3\\[5]CH_3\end{cases} \longrightarrow C_6H_3\begin{cases}[1]CO_2H\\[3]CH_3\\[5]CH_3\end{cases} \longrightarrow C_6H_3\begin{cases}[1]CO_2H\\[3]CO_2H\\[5]CH_3\end{cases} \longrightarrow C_6H_3\begin{cases}[1]CO_2H\\[3]CO_2H\\[5]CO_2H\end{cases}$$

Mesitylene — Mesitylenic acid — Uvitinic acid — Trimesinic acid.

Under the influence of ozone, mesitylene gives a triozonide, which is split by water with formation of methyl-glyoxal (A. **348,** 370).

Pseudo-cumol, [1, 3, 4]-*trimethyl-benzol,* is also contained in coal-tar. It is separated from mesitylene by means of the less soluble sulpho-acid (B. **9,** 258). Also formed from bromo-p-xylol, and 4-bromo-m-xylol, which determines its constitution.

Hemi-mellithol, [1, 2, 3]-*trimethyl-benzol,* occurs in coal-tar (B. **42,** 3603); prepared from isodurylic acid $C_6H_2(CH_3)_3COOH$, and from 2-bromo-m-xylol with CH_3I and Na.

The three ethyl-toluols have been obtained from the three bromo-toluols with ethyl halides and Na. All these isomers are found in coal-tar (B. **42,** 3613).

p-Ethyl-toluol, m.p. 162°, has been obtained from p-methyl-styrol and from p-cresyl-ketone by reduction (B. **28,** 2648; **36,** 1637).

n-Propyl-benzol, from bromo-benzol, n-propyl bromide or iodide and Na; from benzyl chloride and zinc ethyl; from benzene, n-propyl bromide, and Al_2Cl_6 at −2° (B. **24,** 768); and from propenyl-benzol $C_6H_5CH:CHCH_3$ with Na and alcohol (B. **36,** 622). Also found in coal-tar.

Isopropyl-benzol, *cumol,* $C_6H_5CH(CH_3)_2$, first obtained by distillation of cuminic acid $(CH_3)_2CHC_6H_4COOH$ with lime. Synthetically from benzal chloride and $Zn(CH_3)_2$; and from benzene, isopropyl chloride or bromide, and Al chloride. Since heat transposes n-propyl bromide, with Al_2Cl_6, into isopropyl bromide, the Al synthesis gives isopropyl-benzol even when n-propyl bromide is used, unless the process is conducted in the cold. Cumol is best prepared synthetically by the reduction of isopropenyl-benzol $C_6H_5C(CH_3):CH_2$ with Na and alcohol

(B. **35,** 2640). In the animal body cumol is oxidised to propyl-phenol (B. **17,** 2551).

In the hydrocarbons $C_{10}H_{14}$ theory predicts 22 isomers:

$C_6H_2(CH_3)_4$	$C_6H_3\{C_2H_5, (CH_3)_2$	$C_6H_4\{C_3H_5, C_2H_5$	$C_6H_4\{C_3H_7, CH_3$	$C_6H_5.C_4H_9$
3 isomers	6 isomers	3 isomers	6 isomers	4 isomers.

(*a*) **Tetramethyl-benzols** $C_6H_2(CH_3)_4$.—The three possible isomers are known:

Durol, [1, 2 4, 5]- or *sym. tetramethyl-benzol,* is found in coal-tar (B. **18,** 3034). Prepared from 6-bromo-pseudo-cumol and 4, 6-dibromo-m-xylol with CH_3I and Na; from toluol and pseudo-cumol with CH_3Cl and Al chloride (B. **35,** 868); and from penta- and hexamethyl-benzol with Al_2Cl_6. On oxidation it passes into durylic acid and cumidinic acid, thus proving its constitution (B. **11,** 31). Concentrated H_2SO_4 converts durol into hexamethyl-benzol and the sulpho-acids of prehnitol, pseudo-cumol, and isoxylol, which can be separated by means of their amides. Similar behaviour is shown by pentamethyl and penta-ethyl-benzols.

Isodurol, [1, 2, 3, 5]- or *unsym. tetramethyl-benzol,* from bromo-mesitylene, CH_3I and Na (B. **27,** 3441), which proves its constitution; also from camphor and Zn chloride or iodide (B. **16,** 2259). By oxidation it gives 3-isodurylic acid (B. **15,** 1853), and finally, mellophanic acid.

Prehnitol, [1, 2, 3, 4]- or **v-tetramethyl-benzol,** from 2-bromo-pseudo-cumol, and from 2, 4-dibromo-m-xylol, CH_3I and Na (B. **21,** 2821). Oxidised to prehnitylic acid $C_6H_2(CH_3)_3COOH$ (B. **19,** 1214), and prehnitic acid $C_6H_2(COOH)_4$.

(*b*) **Dimethyl-ethyl-benzols:** [1, 2, 4], b.p. 189°, and [1, 3, 4], b.p. 184°; [1, 4, 3], b.p. 185°, from camphor with $ZnCl_2$ and iodine, and from the corresponding dimethyl-vinyl-benzols by reduction (B. **23,** 988, 2349; **36,** 1637); [1, 3, 5], b.p. 185°, from acetone and methyl-ethyl-ketone with SO_4H_2 (B. **18,** 666; **25,** 1533).

(*c*) Three **diethyl-benzols** oxidise first to ethyl-benzoic acids and then to phthalic acids. **p-Diethyl-benzol,** b.p. 183°, has also been obtained from p-ethyl-styrol by reduction (B. **36,** 1633).

(*d*) **Methyl-n-propyl-benzols.**—The most important is the p-compound, cymol. m-Methyl-isopropyl-benzol is found in light resin oil (A. **210,** 10). Also generated on heating *fenchone* (*q.v.*) with phosphorus pentoxide (A. **275,** 157). o-Methyl-isopropyl-benzol has been prepared from o-bromo-cumol with Na, and methyl iodide (B. **34,** 1950).

Cymol, [1, 4]-*methyl-isopropyl-benzol* (see Table, p. 55), found in Roman carraway oil from the seeds of *Cuminum cyminum* besides cuminaldehyde, in the oil from the seeds of *Cicuta virosa,* in thyme oil, eucalyptus oil, and many other etheric oils. Prepared from thymol, carvacrol, or camphor with P_2S_5 (B. **16,** 791, 2259) or P_2O_5 (A. **172,** 307); from turpentine oil, and other terpenes, with withdrawal of 2H, by SO_4H_2 or iodine. We must note the formation of cymol on boiling cumin alcohol with zinc dust, and from citral. Synthetically, cymol is produced from p-brom-isopropyl-benzol, CH_3I and Na, which fixes its constitution (B. **24,** 439, 970, 1362). Cymol has a pleasant

odour. The cymol-sulpho-salt of barium $(C_{10}H_{13}SO_3)_2Ba+3H_2O$, crystallising in shiny scales, is characteristic.

By dilute HNO_3, and chromic acid mixture, cymol is converted into paratoluylic acid and terephthalic acid; but in the animal organism it is oxidised to cuminic acid, also on shaking up with NaHO and air. MnO_4K yields p-oxy-isopropyl-benzoic acid $(CH_3)_2C(OH)C_6H_4COOH$. The action of concentrated HNO_3 upon cymol, produces p-tolyl-methyl-ketone (B. **19,** 588; **20,** R. 373).

(*e*) Butyl-benzols: **n-Butyl-benzol,** b.p. 180°. **Isobutyl-benzol,** b.p. 167°. **Sec.-butyl-benzol,** b.p. 174°, by reduction of sec.-butenyl-benzol $C_6H_5C(CH_3):CHCH_3$ (C. 1900, I. 591; B. **35,** 2642). **Tert.-butyl-benzol,** b.p. 167°. The latter is not attacked by bromine in sunlight, in the cold (B. **23,** 2412; **27,** 1610).

Higher Homologues of Toluol.

We may mention the following:

Hydrocarbons $C_{11}H_{16}$.—**Pentamethyl-benzol** and **hexamethyl-benzol** from toluol, xylol, mesitylene, CH_3Cl, and Al_2Cl_6 (B. **20,** 896). For behaviour with SO_4H_2 see Durol. **[1, 3, 5]-Diethyl-methyl-benzol,** b.p. 200°, from a mixture of acetone and methyl-ethyl-ketone, with sulphuric acid. **[1, 2, 4, 5]-Trimethyl-ethyl-benzol,** *ethyl-pseudo-cumol,* b.p. 207° (B. **25,** 1530; **36,** 1641). **Ethyl-mesitylene,** b.p. 208° (B. **29,** 2459; **36,** 1642). **[1, 3]-Methyl-tert.-butyl-benzol,** b.p. 185°–187°, occurs in resin essence, the distillation product of fir resin; prepared from toluol, isobutyl bromide, and Al_2Cl_6. Its trinitro-derivative forms *artificial musk* (B. **27,** 1606). The isomeric **p-tert.-butyl-toluol,** b.p. 190°, is obtained from toluol and isobutyl alcohol with fuming sulphuric acid (C. 1898, I. 450). Amyl-benzols, see C. 1899, I. 776; B. **35,** 2644.

Hydrocarbons $C_{12}H_{18}$.—**Hexamethyl-benzol,** by polymerisation of crotonylene with SO_4H_2; by heating xylidin chloride with methyl alcohol to 300°; also by analogy with durol. Insoluble in SO_4H_2, as it cannot form a sulpho-acid. Potassium permanganate oxidises it to benzol-hexacarboxylic acid $C_6(COOH)_6$, mellithic acid. **p-Di-n-propyl-benzol,** b.p. 219°, from p-dibromo-benzol, and **p-n-Propyl-isopropyl-benzol,** b.p. 212°, from cumyl chloride $ClCH_2.C_6H_4CH(CH_3)_2$ with $Zn(C_2H_5)_2$. These bodies both yield n-propyl-benzoic acid, isomeric with cuminic acid, on oxidation with HNO_3. **Propyl-mesitylene,** b.p. 221° (B. **29,** 2459); **Isobutyl-mesitylene,** b.p. 228°; **iso-amyl-mesitylene,** b.p. 241°, by reduction of the corresponding acyl-mesitylenes (B. **37,** 1715).

[1, 3, 5]-Triethyl-benzol, b.p. 218°, from ethyl-methyl-ketone with sulphuric acid; from benzene, ethyl chloride, and Al_2Cl_6 we obtain, besides the sym. form, the as- or [1, 2, 4]-triethyl-benzol, b.p. 218°, which can be separated from the former by the greater stability of its sulpho-acid, against phosphoric acid, and can also be obtained by reduction of diethyl-vinyl-benzol (*J. pr. Ch.* 2, **65,** 394; B. **36,** 1634). **[1, 2, 3, 4]-Tetraethyl-benzol,** b.p. 251°. **[1, 2, 4, 5]-Tetraethyl-benzol,** m.p. +13°, b.p. 250° (B. **36,** 1635). **Pentaethyl-benzol. Hexaethyl-benzol** from C_6H_6, C_2H_5Br or ether and Al_2Cl_6 (B. **16,** 1745; **21.** 2819). Optically active **Hexyl-benzols** $C_6H_5CH_2CH_2CH(CH_3)C_2H_5$,

b.p. 220°, and $C_6H_5CH(CH)_3.CH_2.CH(CH_3)_2$, b.p. 197°, s. B. **37**, 654, 2308. Active **p-Isopropyl-hexyl-benzol** $C_3H_7.C_6H_4CH_2.CH_2.CH(CH_3)$, C_2H_5, b.p. 265° (B. **38**, 2313). **Heptyl-benzol** $C_6H_5CH(CH_3)CH_2$ $CH_2C(CH_3)_2$ (B. **35**, 2645). **Tert.-p-butyl-ethyl-benzol**, b.p. 209°, from p-butyl-aceto-phenone (C. 1905, I. 29). **Tert.-p-dibutyl-benzol**, m.p. 76°, b.p. 236° (C. 1904, II. 1112).

By Fittig's method the following mono- and di-alkyl-benzols with long side chain were obtained from bromo-benzol and bromo-toluol:— **n-Octyl-benzol**, b.p. 262°. **Cetyl-benzol** $C_6H_5.C_{16}H_{33}$, m.p. 27°, b.p.$_{15}$ 230°. **o-Methyl-cetyl-benzol**, m.p. 8°–9°, b.p.$_{15}$ 239°. **m-Methyl-cetyl-benzol**, m.p. 10°–12°, b.p.$_{15}$ 237°. **p-Methyl-cetyl-benzol**, m.p. 27°, b.p.$_{15}$ 240°. **Octo-decyl-benzol**, m.p. 36°, b.p.$_{15}$ 249° (B. **21**, 3182).

2. Halogen Derivatives of the Benzene Hydrocarbons.

A. Halogen Substitution Products of Benzene.

As a cyclic triolefin, benzene, in sunlight, adds six atoms Cl or Br, thus forming benzene hexachloride and benzene hexabromide—bodies which, as derivatives of cyclohexane, are treated later in connection with hexahydro-benzol. But the H atoms attached to the benzene nucleus are also easily replaced by chlorine and bromine, more easily than the H atoms of the paraffins.

Properties and Behaviour.—The halogen benzols are partly colourless liquids, partly colourless crystalline compounds. They have a feeble, but not unpleasant, odour. They are not soluble in water, but easily in other solvents, and volatilise without decomposition. Of the dihalogen benzols the para-compounds are solid, at ordinary temperatures. They melt at higher temperatures than the ortho- and meta-compounds, but boil at lower temperatures.

There is a remarkably close attachment of the halogen atoms to the benzene nucleus. They do not make a double decomposition (or only with great difficulty) with alkaline hydroxides, ammonia, potassium cyanide, etc. (B. **18**, 335; **20**, R. 712); but metals like Mg, Na, and Cu extract halogens, especially from benzol bromides and iodides. This is of importance for the synthesis of homologous benzene hydrocarbons. There is a notable facility of reaction of chloro-, bromo-, and iodo-benzol with piperidin, forming *phenyl-piperidin*; prolonged heating with dimethyl-amine leads to dimethyl-aniline (B. **21**, 2279; C. 1898, II. 478). Small quantities of powdered copper, or copper salts, which act catalytically, greatly favour the transformation with ammonia, and amines (C. 1909, I. 475; B. **40**, 4541). Sodium amalgam in alcoholic solution, HI (C. 1898, II. 422; *J. pr. Ch.* 2, **65**, 564), and phosphorus, as well as Ni and H at 270° (C. 1904, I. 720), reduce the halogen benzols to benzene.

Fluoro-benzols are formed from benzol-diazo-piperididene by adding hydrofluoric acid (Wallach, A. **243**, 221)

$$C_6H_5N{=}N{-}NC_5H_{10}+2HFl=C_6H_5Fl+N_2+NH.C_5H_{10}.HFl.$$

They are formed from the benzol-diazonium chlorides, sulphates, and fluorides (*q.v.*) by decomposition with aqueous solutions of HF (C. 1898, I. 1224; 1900, I. 145; 1905, I. 1230).

Fluoro-benzol C_6H_5F, m.p.—41·2°, b.p. 85°, D^4_{20} 1·0236, has also been obtained by heating fluoro-benzoic acid with HCl.

p-Difluoro-benzol $C_6H_4[1,4]F_2$, b.p. 88°, D 1·11.

Chloro-benzols.—Modes of formation :—(1) Free chlorine acts but slowly upon benzene. Its action is assisted by I, $MoCl_5$, VCl_4 (C. 1904, I. 87), $FeCl_3$ (C. 1899, II. 287), or $AlCl_3$. Chlorination can also be accomplished with $PbCl_4.2NH_4Cl$ (C. 1903, I. 283, 570).

(2) The hydroxyl group of the phenols is chlorinated with difficulty by PCl_5; in the nitro-phenols this replacement is easier.

(3) A very important process for forming chloro-benzols, and aromatic halogen derivatives generally, is based upon the transformations of the so-called diazo-compounds, obtained from amido-compounds, the reduction products of nitro-compounds. These reactions involve no atomic displacement, the chlorine taking the place previously occupied by the diazo-, amido-, or nitro-group.

Benzol-diazonium-chloride $C_6N_5N_2Cl=C_6H_5Cl+N_2$.

If, therefore, in the di- and poly-substitution products the constitution of one of these bodies is known, the constitution of the others is determined.

Name.	Formula.	M.p.	B.p.	D.
Monochloro-benzol	C_6H_5Cl	−45°	132°	1·128 (0°)
[1, 2]-(o)-Dichloro-benzol	$C_6H_4Cl_2$	..	180°	
[1, 3]-(m)-Dichloro-benzol	..	..	172°	
[1, 4]-(p)-Dichloro-benzol	..	+53°	172°	
[1, 2, 3]-(v)-Trichloro-benzol	$C_6H_3Cl_3$	16°	218°	
[1, 2, 4]-(as)-Trichloro-benzol	..	63°	213°	
[1, 3, 5]-(s)-Trichloro-benzol	..	54°	208°	
[1, 2, 3, 4]-(v)-Tetrachloro-benzol	$C_6H_2Cl_4$	46°	254°	
[1, 2, 3, 5]-(as)-Tetrachloro-benzol	..	50°	246°	
[1, 2, 4, 5]-(s)-Tetrachloro-benzol	..	137°	244°	
Pentachloro-benzol	C_6HCl_5	86°	276°	
Hexachloro-benzol	C_6Cl_6	226°	326°	

In the chlorination of chloro-benzol, p-dichloro-benzol is mostly formed, with but little o-dichloro-benzol (B. **29**, R. 648); p-dichloro-benzol is also obtained from p-quinone (*q.v.*) with PCl_5. Further chlorination of o-, m-, and p-dichloro-benzol yields 1, 2, 4-trichloro- and 1, 2, 4, 5-tetrachloro-benzol (C. 1905, II. 1528). Characteristic, for the dichloro-benzols, is their behaviour on nitrogenation:

o-Dichloro-benzol gives [1, 2]-dichloro-4-nitro-benzol, m.p. 43°
m-Dichloro-benzol „ [1, 3]-dichloro-4-nitro-benzol, „ 32°
p-Dichloro-benzol „ [1, 4]-dichloro-3-nitro-benzol, „ 55°.

Hexachloro-benzol (Julin's " chlorocarbon ") has also been obtained by the thorough chlorination of many alkyl-benzols, and other benzene derivatives (B. **29**, 875). It is also formed on conducting $CHCl_3$ or C_2Cl_4 through an incandescent tube.

Bromo-benzols have been obtained in a manner quite similar to the chloro substitution products, *i.e.* (1) by direct substitution, through bromine carriers, like Al bromide (B. **10**, 971) or a mixture of sulphur bromide and HNO_3 (B. **33**, 2883; C. 1901, II. 750); (2) from phenolene; (3) from diazo-compounds (*q.v.*).

Name.	Formula.	M.p.	B.p.	D.
Monobromo-benzol	C_6H_5Br	−31°	155°	1·517 (0°)
[1, 2]-(o)-Dibromo-benzol	$C_6H_4Br_2$	+ 7·8° *	224°	
[1, 3]-(m)-Dibromo-benzol	..	− 6·5° *	219·4° *	
[1, 4]-(p)-Dibromo-benzol	..	89°	219°	
[1, 2, 3]-(v)-Tribromo-benzol	$C_6H_3Br_3$	87°	..	
[1, 2, 4]-(as)-Tribromo-benzol	..	44°	275°	
[1, 3, 5]-(s)-Tribromo-benzol	..	119°	278°	
[1, 2, 3, 4]-(v)-Tetrabromo-benzol	$C_6H_2Br_4$	..	..	
[1, 2, 3, 5]-(as)-Tetrabromo-benzol	..	98°	329°	
[1, 2, 4, 5]-(s)-Tetrabromo-benzol	..	175°	..	(B. 28, 191)
Pentabromo-benzol	C_6HBr_5	160°	..	(C. 1900, I. 809)
Hexabromo-benzol	C_6Br_6	315°	..	

Of the dibromo-benzols we obtain on bromination of benzene with heat chiefly the p-compounds, more rarely the o-compounds (B. **10,** 1345). Characteristic of the dibromo-benzols, as of the dichloro-benzols, is their behaviour on nitrogenation.

The generation of tribromo-benzols from the three dibromo-benzols has been used for constitution determinations of all these bodies (Körner). Hexabromo-benzol is generated by heating CBr_4 to 300°.

Chloro-bromo-benzols, see C. 1899, I. 835; II. 959.

Iodo-benzols are obtained (1) by heating benzene, iodine, and HI to 200° (Kekulé). The action is represented by the equation (A. **137,** 161):

$$5C_6H_6+4I+IO_3H=5C_6H_5I=3H_2O.$$

(2) By treating benzene with a mixture of I_2S_2 and HNO_3 (B. **33,** 2875; C. 1901, II. 750).

(3) More usually, iodo-benzols are prepared from the corresponding amido-compounds with the help of the diazo-compounds (*q.v.*).

(4) Bromo-benzol may be transformed to iodo-benzol by changing it in ether solution to phenyl-magnesium bromide, and then treating with iodine (C. 1903, I. 318):

$$C_6H_5Br \xrightarrow{Mg} C_6H_5MgBr \xrightarrow{I_2} C_6H_5I+MgBrI.$$

Name.	Formula.	M.p.	B.p.
Iodo-benzol	C_6H_5I	−30°	188°
[1, 2]-(o)-Di-iodo-benzol	$C_6H_4I_2$	+27°	286°
[1, 3]-(m)-Di-iodo-benzol	..	40°	285°
[1, 4]-(p)-Di-iodo-benzol	..	129°	285°
[1, 2, 3]-(v)-Tri-iodo-benzol	$C_6H_3I_3$	116° *	
[1, 2, 4]-(as)-Tri-iodo-benzol	..	91·4° *	see B. **34,** 3343; C. 1901, II. 535
[1, 3, 5]-(s)-Tri-iodo-benzol	..	184·4°	
[1, 2, 3, 4]-(v)-Tetra-iodo-benzol	$C_6H_2I_4$	136° *	
[1, 2, 4, 6]-(as)-Tetra-iodo-benzol	..	148°	
[1, 2, 4, 5]-(s)-Tetra-iodo-benzol	..	254° *	
Penta-iodo-benzol	C_6HI_5	172°	
Hexa-iodo-benzol	C_6I_6	140°–150°	

Hexa-iodo-benzol C_6I_6 forms during thorough iodination of benzol-carboxylic acids (benzoic acid, terephthalic acid) with iodine and

fuming sulphuric acid. It forms reddish-brown needles which melt and decompose at 140°–150° (B. **29**, 1631).

1, 3, 5-Tri-iodo-2-chloro-benzol (C. 1907, I. 632). About **Bromo-iodo-benzols** (B. **29**, 1405; C. 1899, II. 371). **1, 3, 5-Tri-iodo-2, 4, 6-tribromo-benzols** $C_6Br_3I_3$, m.p. 322° (C. 1898, II. 972).

Iodide chlorides; Iodoso-benzol; Iodo-benzol; Diphenyl-iodonium hydroxide.—The iodo-benzols and their homologues, by the action of chlorine or substances easily liberating chlorine, are transformed into iodide-chlorides, *e.g.* phenyl iodide-chloride $C_6H_5ICl_2$ (Willgerodt, 1886). These contain chlorine bound to iodine, and may therefore be referred to iodine trichloride ICl_3. The formation of these peculiar compounds is useful for the characterisation of iodinated benzene derivatives. The iodo-chlorides are easily changed into iodoso-benzols, and should be regarded as the chlor-anhydrides of the latter. From the iodoso-benzols we arrive through oxidation at the iodo-benzols, *e.g.* $C_6H_5IO_2$. From iodoso- and iodo-benzol we finally obtain the strongly basic diphenyl-iodonium hydroxide.

Phenyl-iodo-chloride $C_6H_5ICl_2$, yellow needles, formed on conducting chlorine through a solution of iodo-benzol in chloroform. By heating it is changed into p-iodo-chloro-benzol with liberation of chlorine (C. 1907, I. 1198; II. 43). Shaken up with water and alkalies or other bases, it yields iodoso-benzol:

$$C_6H_5ICl_2+2KOH=C_6H_5IO+2KCl+H_2O.$$

Iodoso-benzol C_6H_5IO is an amorphous substance exploding about 210°; treated with acidulated KI solution, it gives up its oxygen with liberation of the equivalent quantity of iodine:

$$C_6H_5IO+2KI+2CH_3COOH=C_6H_5I+2CH_3COOK+2I+H_2O.$$

It has a basic character, and yields salts derivable from the hypothetical hydrate $C_6H_5I(OH)_2$, like $C_6H_5I(OOCCH_3)_2$; we must therefore regard $C_6H_5ICl_2$ as an iodoso-benzol chloride.

Iodo-benzol $C_6H_5IO_2$, by heating iodoso-benzol by itself, or by boiling in water:

$$2C_6H_5IO=C_6H_5I+C_6H_5IO_2;$$

also by oxidation of iodoso-benzol with hypochlorous acid, or treatment of phenyl-iodo-chloride with bleaching-powder solution (B. **29**, 1567; cp. B. **33**, 853). It is also formed direct from iodo-benzol by oxidation with K persulphate and concentrated H_2SO_4 (Caro's reagent, B. **33**, 533). Iodo-benzol explodes at 227°–230°. It exhibits the behaviour of a super-oxide.

With concentrated HF, iodo-benzol yields **benzol-iodo-fluoride** $C_6H_5IOF_2$, which with water regenerates iodo-benzol (B. **34**, 2631).

Diphenyl-iodonium hydroxide $(C_6H_5)_2IOH$ is only known in aqueous solution. Generated by shaking up a mixture of iodoso- and iodo-benzol with moist silver oxide, according to the equation

$$C_6H_5IO+C_6H_5IO_2+AgOH=(C_6H_5)_2I.OH+IO_3Ag.$$

Its iodide is formed on boiling iodo-benzol with KI solution (B. **29**, 2008). Diphenyl-iodonium hydroxide has a strong alkaline reaction, and forms salts resembling those of thallium; the carbonate and

nitrate are very soluble. The chloride and bromide form white precipitates.

Diphenyl-iodonium iodide $(C_6H_5)_2I.I$ is polymeric with iodo-benzol. It forms yellow needles soluble in alcohol with difficulty. They melt at 175°–176°, forming iodo-benzol (V. Meyer, B. **27**, 1592; **28**, R. 80).

Fat-aromatic iodonium salts are obtained by transformation of acetylene-silver chloride with aromatic iodo-chlorides:

$$2C_6H_5ICl_2 + HC{\equiv}CAg,AgCl = ClHC : CCl\diagdown\!\diagup I{-}Cl + C_6H_5I + 2AgCl.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C_6H_5\diagup$$

Dichloro-vinyl-phenyl-iodonium chloride, m.p. 174°. Bromide decomposes at 162°. The free base is unstable (A. **369**, 132).

A number of homologous and substituted iodo-chlorides, iodoso- and iodo-benzols, and iodonium hydroxides have been prepared (see C. 1900, I. 761; 1902, II. 1196; B. **34**, 3406, 3666; **37**, 1301; **39**, 269).

B. Halogen Derivatives of the Alkyl-Benzols.

Under the same conditions as in benzene itself, in the cold, in the presence of I, $MoCl_5$, VCl_4, $FeCl_3$, sulphur bromide, and HNO_3 (B. **33**, 2885), so in the alkyl-benzols the chlorine and bromine atoms enter almost solely into the benzene residue, and aromatic substitution products are formed. Thus, toluol yields:

$$C_6H_5CH_3 \longrightarrow C_6H_4Cl.CH_3 \longrightarrow C_6H_3Cl_2CH_3, \text{ etc.}$$
$$C_6H_5CH_3 \longrightarrow C_6H_4BrCH_3 \longrightarrow C_6H_3Br_2CH_3, \text{ etc.}$$

But on conducting Cl and Br through the boiling alkyl-benzols, hardly anything but the hydrogen of the side chain is replaced, and aliphatic substitution products are obtained. Thus, from toluol

$$C_6H_5CH_3 \longrightarrow \underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \longrightarrow \underset{\text{Benzal chloride}}{C_6H_5CHCl_2} \longrightarrow \underset{\text{Benzo-trichloride}}{C_6H_5CCl_3}$$

are obtained, corresponding to

$$\underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \longrightarrow \underset{\text{Ethylidene chloride}}{CH_3CHCl_2} \longrightarrow \underset{\text{Methyl chloroform.}}{CH_3CCl_3}$$

These are dealt with in connection with the corresponding oxygenated compounds:

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} \longrightarrow \underset{\text{Benzaldehyde}}{C_6H_5CHO} \longrightarrow \underset{\text{Benzoic acid}}{C_6H_5CO_2H}$$

into which they can be easily converted, and from which they can be obtained by means of PCl_5.

In sunlight, Cl and Br produce substitutions of the aliphatic side chains of the lower homologues, even when cold (B. **20**, R. 530; cp. B. **35**, 868). Isopropyl-benzol is transformed by Cl, at boiling-point, into p-chlorisopropyl-benzol (B. **26**, R. 771). PCl_3 also attacks the alkyles of the alkyl-benzols when hot. In this and many other reactions the presence of other substituents, in the benzene nucleus, exercises an impeding influence (C. 1898, I. 367, 1019).

The two other methods for preparing the halogen derivatives of benzene, viz. the action of halogen phosphorus compounds upon oxy-benzols, and the transformation of the corresponding diazo-compounds, give alkyl-benzols, with substitution of halogens in the benzene residue. A substitution can take place both in the aromatic and the aliphatic residue of the same alkyl-benzol. The halogen atoms entering the side chain are always capable of reaction. They freely exchange for radicles, whereas the halogen atoms entering the benzene residue are very strongly bound. The aromatic monohalogen derivatives of the alkyl-benzols, especially the bromalkyl-benzols, are often used for building up higher alkyl-benzols by Fittig's method. Of some importance for recognising the constitution is the oxidation of the side chains to carboxyl groups, which enables us also to determine the halogen atoms in the side chains.

With sodium amalgam in alcoholic solution, or with HI, the halogens are replaced by hydrogen.

Of the very numerous aromatic halogen substitution products of this kind we may here enumerate the simplest representatives of the monohalogen toluols :

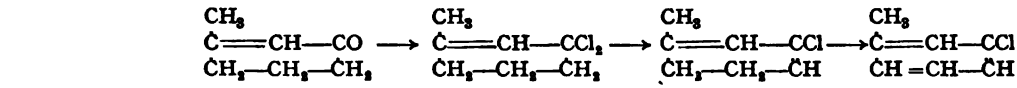
Name.	Formula.	M.p.	B.p.
[1, 2]-, o-Fluoro-toluol .	$CH_3[1]C_6H_4[2]F$	..	114° (C. 1906, II. 1830)
[1, 3]-, m-Fluoro-toluol .	$CH_3[1]C_6H_4[3]F$	..	115°
[1, 4]-, p-Fluoro-toluol .	$CH_3[1]C_6H_4[4]F$	..	116°
[1, 2]-, o-Chloro-toluol .	$CH_3[1]C_6H_4[2]Cl$	−34°	156°
[1, 3]-, m-Chloro-toluol .	$CH_3[1]C_6H_4[3]Cl$	−48°	150°
[1, 4]-, p-Chloro-toluol .	$CH_3[1]C_6H_4[4]Cl$	+ 7°	163°
[1, 2]-, o-Bromo-toluol .	$CH_3[1]C_6H_4[2]Br$	−26°	181°
[1, 3]-, m-Bromo-toluol .	$CH_3[1]C_6H_4[3]Br$	−40°	183°
[1, 4]-, p-Bromo-toluol .	$CH_3[1]C_6H_4[4]Br$	+28°	184°
[1, 2]-, o-Iodo-toluol .	$CH_3[1]C_6H_4[2]I$	..	204°
[1, 3]-, m-Iodo-toluol .	$CH_3[1]C_6H_4[3]I$	..	204°
[1, 4]-, p-Iodo-toluol .	$CH_3[1]C_6H_4[4]I$	35°	211°

o-, m-, and p-Fluoro-toluols have been prepared by the same methods as fluoro-benzol. On chlorinating or brominating toluol in the cold, or in the presence of iodine or $FeCl_3$, para- and ortho-compounds are produced, in nearly equal quantities. The p-chloro-toluol may be separated from the o-compound by heating to 150° with sulphuric acid, when the o-compound forms a sulpho-acid.

All the monochloro-, monobromo-, and mono-iodo-toluols may be obtained pure by decomposition of the diazo-compounds (*q.v.*) obtained from the three amido-toluols or toluidinenes. The o- and p-chloro-toluols are easily obtained from the corresponding toluidins. The m-bromo-toluol has also been obtained by brominating aceto-p-toluidin to m-brom-aceto-p-toluidin and then replacing the amido-group by hydrogen.

The m-chloro-toluol has also been obtained from 3-methyl-Δ_2-keto-R-hexene, easily prepared from methylene-diaceto-acetic ester. In this process tetrahydro-m-dichloro-toluol is first prepared by means of PCl_5, and then it splits into HCl and dihydro-m-chloro-toluol.

Bromine withdraws two H atoms from this body, and m-chloro-toluol is formed (B. **27**, 3019) :



If we start from ethylidene-binaceto-acetic ester, we obtain [1, 3, 5]-chloro-m-xylol (B. **29**, 310); and [1, 3, 6]-chloro-cymol has been similarly obtained from menthone or keto-hexahydro-p-cymol (B. **29**, 314).

The iodoso- and iodo-compounds corresponding to p-iodo-toluol are known (B. **26**, 358 ; **27**, 1903).

For the halogen toluols their transformation into solid nitro-halogen toluols, and their oxidation to the halogen benzoic acids of known constitution, are characteristic. Chromic acid oxidises the m- and p-halogen toluols to the corresponding carboxylic acids, but it completely burns up the o-halogen toluols. By boiling with dilute HNO_3, by potassium permanganate or potassium ferricyanide, all the three isomers, including the ortho-compounds, are converted into carboxylic acids.

Of *aromatic di-halogen toluols* with similar halogens six isomers are possible. The six isomeric dichloro-toluols are known (B. **29**, R. 867). They are isomeric with benzal chloride $C_6H_5CHCl_2$, and the three chloro-benzyl chlorides $ClC_6H_4CH_2Cl$. For particulars of the higher chlorination products of toluol, see C. 1902, II. 1178 ; 1904, II. 1292, etc. The six isomeric dibromo-toluols and di-iodo-toluols have all been obtained (C. 1910, I. 525). Pentabromo-toluol is prepared from suberane and bromine. The six isomeric tribromo-xylols are all known (C. 1906, II. 1831).

The following table contains the easily prepared bromo-derivatives of polymethyl-benzols :

Name.	M.p.	B.p.
[1, 2, 4]-Bromo-o-xylol	− 2°	214°
[1, 3, 4]-Bromo-m-xylol	..	203°
[1, 2, 4]-Bromo-p-xylol	+ 9°	200°
Tribromo-hemimellithol	245°	..
[1, 2, 4, 3]-Monobromo-pseudocumol	..	237°
[1, 2, 4, 3, 6]-Dibromo-pseudocumol	64°	293°
Tribromo-pseudocumol	224°	..
Monobromo-mesitylene	− 1°	225°
Dibromo-mesitylene	+60°	285°
Tribromo-mesitylene	224°	..
Monobromo-prehnitol	30°	265°
Dibromo-prehnitol	210°	..
Monobromo-isodurol	..	253°
Dibromo-isodurol	209°	..
Monobromo-durol	61°	262°
Dibromo-durol	199°	317°
Bromo-pentamethyl-benzol	160°	289°

It is also remarkable that concentrated sulphuric acid can transfer bromine atoms instead of alkyl groups. It thus converts monobromo-durol first into dibromo-durol and then into lurol (B. **25**, 1526).

A number of iodinated alkyl-benzols have, like iodo-benzol itself, been prepared by means of sulphur iodide and HNO_3 (see B. **33**, 2875).

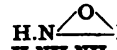
Concerning the influence of alkyl groups in the "reverse substitution" of iodine in iodinated benzols, see *J. pr. Ch.* 2, **65**, 564.

3. Nitrogen Derivatives of Benzene Hydrocarbons in which the nitrogenated residue is connected with the benzene nucleus by nitrogen linking.

These compounds may be classified by the number of nitrogen atoms contained in the residues. The first class is formed by compounds in which the nitrogen group only contains one nitrogen atom. This is headed by the *nitro*-compounds, so characteristic of the benzene derivatives in general, which form the bases for obtaining the succeeding groups. Then come the *amido*-compounds, which comprise the generators of many coal-tar dyes and aromatic bodies of therapeutic importance. A link between both groups is formed by the *nitroso*- and the *β-hydroxylamine* compounds.

The second class is formed by the compounds in which the nitrogenated residue contains two or more N atoms mutually linked. Two N atoms are carried by the *nitro-amines*, the *nitroso-β-hydroxyl-amines*, the *nitrosamines*, the *azoxy*-compounds, the *hydrazins*, the *diazo-* and the *azo*-compounds. Three N atoms are carried by the *nitroso*-hydrazins, the *diazo-amido*-compounds, and the *azo-imido*-compounds; four N atoms by the *diazo*-hydrazides or buzylene compounds, and the tetrazones; five N atoms by the *bis-diazo-amido*-compounds; and eight N atoms by the *bis-diazo-tetrazones* or *octazones*.

Our knowledge of some of these classes of bodies has acquired the greatest importance, even for the chemistry of the inorganic nitrogen compounds. If we imagine these nineteen groups of aromatic nitrogen compounds derived from the inorganic nitrogen compounds obtained by replacing the aromatic residues by hydrogen, then out of the nineteen, only six occur free or in inorganic compounds, and these are printed in heavy type in the following list:

1.	*Nitro*-compounds	derived from	**$H.NO_2$**
2.	*Nitroso*-compounds	,, ,,	H.NO
3.	*β-Hydroxylamine*-compounds	,, ,,	**H.NHOH**
4.	*Amido*-compounds	,, ,,	**$H.NH_2$**
5.	*Nitro-amines*	,, ,,	**$H.NH.NO_2$**
6.	*Nitroso-β-hydroxylamines*	,, ,,	H.N(OH).NO
7.	*Nitrosamines*	,, ,,	H.NH.NO
8.	*Diazo*-compounds	,, ,,	H.N=N.OH H.NH.NO or H.N(OH) : N
9.	*Azo*-compounds	,, ,,	H.N=N.H
10.	*Azoxy*-compounds	,, ,,	
11.	*Hydrazins*	,, ,,	**$H.NH.NH_2$**
12.	*Nitroso-hydrazins*	,, ,,	$H.N(NO).NH_2$
13.	*Diazo-amido*-compounds	,, ,,	$H.N=N.NH_2$
14.	*Diazo-oxy-amido*-compounds	,, ,,	H.N=N—NHOH
15.	*Diazo-imido*-compounds	,, ,,	
16.	*Diazo-hydrazo-* or *Buzylene* compounds	,, ,,	$H.N=N.NH.NH_2$
17.	*Tetrazones*	,, ,,	$H.NH.N=N.NH_2$
18.	*Bis-diazo-amido*-compounds	,, ,,	H.N=N—NH—N=N.H
19.	*Bis-diazo-tetrazone* or *Octazone*	,, ,,	H.N : N.NH.N : N.NH.N : NH.

The first three groups will be dealt with in the succession shown, but the others will be arranged by their genetic rather than their systematic relations, as follows :—Nitroso-β-hydroxylamines ; Amido-compounds ; Nitroso-amines ; Nitro-amines ; Diazo-compounds ; Diazo-amido-compounds ; Bis-diazo-amido-compounds ; Diazo-oxy-amido- and Azo-imido-compounds ; Azoxy- and Azo-compounds ; Hydrazines ; Nitroso-hydrazines ; Tetrazones ; Diazo-hydrazo- or Buzylene compounds ; and Octazones.

1. Nitro-Derivatives of Benzene and the Alkyl-Benzols.

Benzene and the alkyl-benzols which contain H atoms attached to the nucleus easily give nitro-derivatives under the action of nitric acid :

$$C_6H_6+NO_2OH=C_6H_5NO_2+H_2O.$$

In these compounds of a more or less yellow colour the nitrogen of the nitro-group is directly linked with a carbon atom, as in nitro-methane, for on reduction we obtain amido-compounds :

$$C_6H_5NO_2+6H=C_6H_5NH_2+2H_2O.$$

In the previous chapter it was stated that all the H atoms of benzene may be replaced by chlorine and bromine. This does not apply to the nitro-groups. The two first nitro-groups enter without difficulty, but the third encounters more resistance, and it has not been found possible to introduce more than three nitro-groups into a benzene derivative.

A mixture of one part HNO_3 and two parts H_2SO_4 acts more energetically than HNO_3 alone, as the sulphuric acid withdraws water. Di- and trinitro-products are mostly obtained thus. A less complete nitrogenation is attained by first dissolving in glacial acetic acid and chloroform (B. **42**, 4151).

The more alkyl groups are contained in a benzene hydrocarbon, the more easily it is nitrogenated. The production of nitro-phenols during such nitrogenation may be explained by assuming an addition of HNO_3 to double links of the benzene ring, and the liberation of HNO_2 on the one hand and H_2O on the other (B. **24**, R. 721 ; **42**, 4152). Such unstable addition products may also be the cause of the dark-brown colouring at first observed during nitrogenation. On heating with dilute HNO_3 the nitro-group enters the aliphatic side chain. Such compounds are dealt with later in connection with the corresponding alcohols (B. **27**, R. 193 ; C. 1899, I. 1237).

An admirable means of nitrogenation has been discovered in benzoyl and acetyl nitrate, suitable for some cases (B. **39**, 3798 ; C. 1907, I. 1025). It avoids the generation of water which accompanies nitrogenation with HNO_3 :

$$C_6H_6+C_6H_5COONO_2=C_6H_5NO_2+C_6H_5COOH.$$

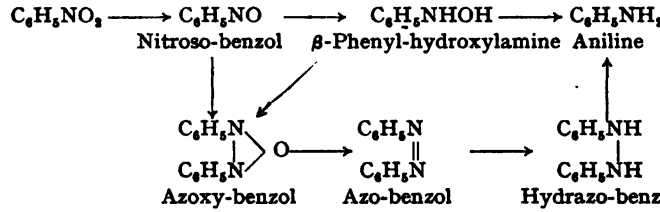
The action of Al_2Cl_6 upon the hydrocarbon mixed with ethyl nitrate can also produce nitro-compounds (C. 1908, II. 403).

From the aromatic amines obtained by reduction of the nitro-compounds the latter may be recovered through the intermediary of the diazo-compounds, the nitrites of which yield nitro-bodies when treated with cuprous oxide. Nitro-bodies have also been obtained by direct

oxidation from amines, *e.g.* nitro-benzol from aniline with K permanganate, in which process β-phenyl-hydroxylamine and nitroso-benzol have been obtained as intermediate products (B. **32,** 1675).

Properties and Behaviour.—The nitro-hydrocarbons are only slightly soluble in water, but they are soluble in concentrated HNO_3, and are precipitated from this solution by water. They are easily dissolved in alcohol, ether, glacial acetic acid, etc. The nitro-products melt at rather a higher temperature than the corresponding bromine derivatives.

Of greater importance is the easy reduction of the nitro-compounds. As intermediate products of the reduction to amido-compounds the nitroso-compounds and the β-phenyl-hydroxylamines have been retained. Both combine, under the influence of an alkali, to azoxy-compounds, which are further reduced to azo- and hydrazo-compounds. These genetic relations are represented by the scheme :



During the electrolytic reduction of nitro-bodies dissolved in sulphuric acid we obtain, besides amido-hydrocarbons, amido-phenols, by transposition of the unstable β-phenyl-hydroxylamines (B. **29,** R. 230). In HCl solution p-chloraniline is formed by a similar process (B. **29,** 1894 ; C. 1907, I. 463).

About the electrolytic reduction of nitro-bodies, see also C.1 901, I. 105, 149 ; B. **38,** 4006 ; A. **355,** 175, etc.

The easy reduction of nitro-bodies to substances useful in the manufacture of coal-tar dyes has given them the position of important and indispensable intermediate products.

By oxidation with alkaline K ferricyanide solution, the polynitro-benzols are easily converted into polynitro-phenols. Nitro-benzol, on heating with powdered caustic potash, yields o-nitro-phenol and azoxy-benzol ; m-nitro-toluol similarly yields m-nitro-o-cresol ; and m-dinitro-benzol yields 2, 4-dinitro-phenol (B. **32,** 3486 ; **34,** 2444 ; C. 1901, I. 149).

By heating with HCl to 200°–300° the nitro-groups are replaced by chlorine in many polynitro-hydrocarbons, and in some cases there is a further chlorination (B. **29,** R. 594).

NITRO-BENZOLS.—The melting-points and boiling-points of the known nitro-benzols are shown in the following table :

Name.	Formula.	M.p.	B.p.
Nitro-benzol . . .	$C_6H_5NO_2$	+5·72°	209° (C. 1897, II. 547)
[1, 2]-, o-Dinitro-benzol .	$C_6H_4(NO_2)_2$	116°	319° (773 mm.)
[1, 3]-, m-Dinitro-benzol .		90°	303° (771 mm.)
[1, 4]-, p-Dinitro-benzol .		172°	299° (777 mm.)
[1, 2, 4]-, as-Trinitro-benzol	$C_6H_3(NO_2)_3$	57°	..
[1, 3, 5]-, s-Trinitro-benzol .		121°	..
[1, 2, 3, 5]-Tetranitro-benzol	$C_6H_2(NO_2)_4$	116°	..

Nitro-benzol $C_6H_5NO_2$ was discovered in 1834 by Mitscherlich (*Pogg. Ann.* **31,** 625), on treating benzene with nitric acid. It is also formed during the oxidation of aniline. It is prepared in large quantities industrially, and worked for aniline and azo-benzol. For the industrial preparation of nitro-benzol a mixture of HNO_3 and H_2SO_4 is allowed to flow into benzene in cast-iron tubes, and kept stirred. Nitro-benzol is a yellowish, highly refractive liquid of density 1·20 at 20°, smelling of benzaldehyde or oil of bitter almonds, tasting sweet in dilute aqueous solution, and acting as a poison, especially when its vapour is breathed. Besides the dye industry, nitro-benzol is also employed in the perfume industry, to give soap an odour of oil of bitter almonds. In the laboratory it is often employed as a solvent or an oxidiser (see Rosaniline and Quinolin).

Dinitro-Benzols $C_6H_4(NO_2)_2$.—On prolonged boiling of benzene with fuming HNO_3, or on short heating with HNO_3 and H_2SO_4, m-dinitro-benzol is chiefly formed, together with the o- and p-forms, which are more easily soluble in alcohol (B. **7,** 1372). The *meta*-compound is used in the dye industry for preparing m-phenylene-diamine.

p-Dinitro-benzol is also obtained from p-quinone dioxime by oxidation; and o-dinitro-benzol from the residues of preparation of m-dinitro-benzol by dissolving in twice its weight of boiling HNO_3 and pouring into the five- or sixfold volume of cold HNO_3, whereupon the o-dinitro-benzol separates out in crystals (B. **26,** 266).

The dinitro-benzols are capable of a lopsided reduction to nitro-anilines (*q.v.*), which form the genetic link between phenylene-diamines and dibromo-benzols, as well as phthalic acids.

Ortho-dinitro-benzol crystallises in plates, yields o-nitro-phenol on boiling with NaHO, and o-nitraniline on heating with alcoholic ammonia. Other o-dinitro-compounds behave in a similar manner.

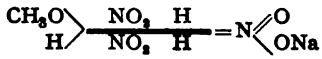
Meta-dinitro-benzol, heated with K ferricyanide and NaHO, or with powdered KHO, yields [1, OH, 2, 4]-dinitro-phenol and [1, OH, 2, 6]-dinitro-phenol. On treating with alcoholic KCy an NO_2 group is replaced by ethoxyl, with entry of a cyanogen group. This produces [2]-nitro-[6]-ethoxy-benzo-nitrile (B. **17,** R. 19). With alkali sulphite it forms, with reduction and sulphuration, m-nitraniline-p-sulpho-acid (B. **29,** 2448).

Para-dinitro-benzol, colourless needles.

By heating the dinitro-benzols with Cl or Br to 200° the nitro-groups are replaced, wholly or partly, by halogens (B. **24,** 3749). On heating them with Na methylate or ethylate, a nitro-group is replaced by a methoxy- or ethoxy-group (C. 1899, I. 1027).

Trinitro-Benzols.—[1, 3, 5]-, *s*-trinitro-benzol, white flakes, from m-dinitro-benzol; or by heating trinitro-benzoic acid; or, synthetically, by oxidation of sodium nitro-malonaldehyde (B. **28,** 2597; C. 1899, II. 609). [1, 2, 4]- or *as*-trinitro-benzol, from p-dinitro-benzol on heating to 180° with HNO_3 and pyro-sulphuric acid. The *s*-trinitro-benzol may be oxidised to picric acid or [1, OH, 2, 4, 6]-trinitro-phenol. With aniline, naphthalin, etc., it forms additive compounds, and similar compounds are furnished by m- and p-dinitro-benzol, trinitro-toluol, etc. (B. **13,** 2346; **16,** 234; **39,** 76; C. 1906, II. 1249). With aqueous alkalies the *s*-trinitro-benzol gives orange-coloured products, probably through the formation of unstable salts; with Na alcoholates

it forms additive compounds of a saline nature, from which water regenerates trinitro-benzol quantitatively. They may be interpreted as salts of " quinolic " nitro-acids :

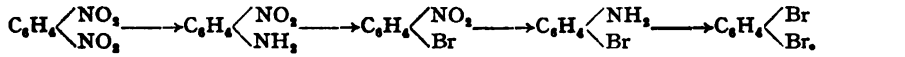


(cp. Quinols, and A. **323**, 219 ; C. 1903, I. 707 ; B. **42**, 2119). On heating with Na alcoholate solution a nitro-group of the *s*-trinitro-benzol is replaced by an alkoxyl group (C. 1901, I. 1289).

as-Tetranitro-benzol $C_6H_2[1, 2, 3, 5](NO_2)_4$, yellow needles, formed from dinitro-dinitroso-benzol by careful oxidation with HNO_3 (B. **34**, 56).

NITRO-HALOGEN-BENZOLS.—Modes of formation:—(1) Nitrogenation of F-, Cl-, Br-, and I-benzols ; p-mononitro-halogen-benzols are formed mostly, also some o-compounds. (2) Treatment of nitro-benzols with bromine or chlorine ; in polynitro-compounds a nitro-group is readily replaced by halogen. (3) Conversion of dinitro-benzols into nitraniline, and replacement of the amido-group by halogens by means of diazo-compounds. (4) Formation from nitro-phenols with PCl_5, producing chloro-nitro-benzols.

The halogen-nitro-benzols form the transition from the dinitro-, nitro-amido-, and diamido-benzols to the halogen-amido- and dihalogen-benzols, and are therefore important for recognising the relations between the various di-substitution products of benzene :



When nitro-groups enter the benzene nucleus in *ortho-* or *para-*position to a halogen atom, this halogen atom requires the capacity of reacting with alkalies, like the halogen alkyls (Vol. I.), while a nitro-group in the *meta*-position does not produce this effect (cp. C. 1903, I. 571). This rule is markedly shown by the behaviour of 1, 2, 4, 6-tetrachloro-3, 5-dinitro-benzol. In this substance only the halogen atoms 2, 4, and 6 can be replaced by the residues NH_2, NHC_6H_5, OC_2H_5, etc., but not the chlorine atom in the m-position with regard to the two nitro-groups (C. 1904, I. 1408). The loosening of the halogen linking is the more marked, the more nitro-groups enter the nucleus, so that 1, 3, 5, 6-trinitro-chloro-benzol or picryl chloride has the character of an acid chloride. In some cases it is not the halogen, but a nitro-group, which is split off; cp. sym. dinitro-chloro- and 1-Cl-3, 4, 6-trinitro-chloro-benzol.

We give here the melting-points of the isomeric mononitro-, fluoro-, chloro-, bromo-, and iodo-benzols :

	[1, 2]	[1, 3]	[1, 4]	
$C_6H_4F(NO_2)$	−8°	+1·69°	+26·5°	(C. 1905, I. 29, 1230)
$C_6H_4Cl(NO_2)$	32·5°	48°	83°	(C. 1898, II. 238 ; 1903, I. 208)
$C_6H_4Br(NO_2)$	43·1°	56°	126°	(B. **29**, 788)
$C_6H_4I(NO_2)$	49°	36°	171·4°	(B. **29**, 1880)

Meta-chloro-nitro-benzol occurs in two physical modifications :— Cooled rapidly after melting, it melts at 23·7° ; but after a short time it changes into the more stable modification melting at 44·2°. A similar behaviour is shown by p-nitro-fluoro-benzol, the two melting-points being 21·5° and 26·5°.

Of the numerous known nitro-halogen-benzols, we may mention the [1, Cl, 3, 4]-dinitro-chloro-benzol, which occurs in three very similar modifications, having melting-points 36·3°, 37°, and 38° (B. **9**, 760; C. 1908, II. 1425).

sym. Dinitro-chloro-benzol, m.p. 59°, formed by chlorination of m-dinitro-benzol. On heating with Na alcoholate solution it exchanges, not the Cl atom, but an NO_2 group for an RO group, forming a nitro-chloro-phenol ether (C. 1900, I. 1115; 1901, I. 1289).

An analogous behaviour is shown by [1, Cl, 3, 4, 6]-**Trinitro-chloro-benzol**, m.p. 116°, obtained by further nitrogenation of [1, Cl, 3, 4]-dinitro-benzol. By the action of ammonia, the nitro-group in the 3-position is replaced by the amido-group (B. **36**, 3953).

[1, 2, 4, 5]-**Dichloro-dinitro-benzol**, m.p. 114°, and [1, 2, 3, 4]-**Dichloro-dinitro-benzol**, m.p. 55°, are formed together during nitrogenation of o-dichloro-benzol. On heating with ammonia, the former exchanges a nitro-group, and the latter a Cl atom for the NH_2 group (B. **37**, 3892).

[1, 3, 5, 4, Cl]-**Trinitro-chloro-benzol-picryl-chloride** $C_6H_2Cl(NO_2)_3$, m.p. 83°, from picric acid by means of PCl_5. The latter, with ammonia solution, gives picramide $C_6H_2(NH_2)(NO_2)_3$, and, on boiling with soda, picric acid is generated.

Picryl bromide $C_6H_2(NO_2)_3Br$, m.p. 123°, from bromo-dinitro-benzol with HNO_3 (C. 1903, I. 963).

Dinitro-dichloro-benzols and their transformation products are described, C. 1902, II. 513; 1903, I. 503, 511; **Dinitro-trichloro-benzol**, m.p. 130°, see B. **29**, R. 1155.

Of the six isomeric dibromo-nitro-benzols, five can be obtained by direct nitrogenation of the three dibromo-benzols:

o-Dibromo-benzol	1.	[1, 2]-Dibromo-4-nitro-benzol, m.p.	58°	Chief product.
	2.	[1, 2]-Dibromo-3-nitro-benzol, „	85·2°	By-product.
m-Dibromo-benzol	1.	[1, 3]-Dibromo-4-nitro-benzol, „	61°	Chief product.
	2.	[1, 3]-Dibromo-2-nitro-benzol, „	82°	By-product.
p-Dibromo-benzol		[1, 4]-Dibromo-1-nitro-benzol, „	85°	

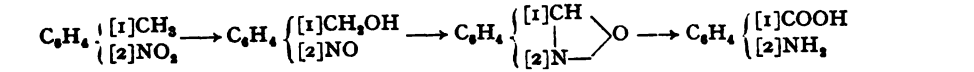
The missing [1, 3]-dibromo-5-nitro-benzol, m.p. 104·5°, was prepared by Körner (J. 1875, 306) from the dibromo-p-nitraniline by eliminating the amido-group. Concerning the transformation of the dibromo-nitro-benzols into tribromo-benzols, and their significance concerning the constitution of the three dibromo-benzols, see above.

Nitro-Toluols.—[1, 2]-, **o-Nitro-toluol** $CH_3[1]C_6H_4[2]NO_2$, two modifications, m.p. −9° and −4°, b.p. 218°; and [1, 4]-, **p-Nitro-toluol** $CH_3[1]C_6H_4[4]NO_2$, m.p. 54°, b.p. 230°, by nitrogenation of toluol. They are separated by fractional distillation, and, on reduction, they yield the industrially important toluidins. On nitrogenation at −55°, 5·5 times as much p- as o-nitro-toluol is produced (B. **26**, R. 362), and even at higher temperatures chiefly p-nitro-toluol is obtained, with fuming nitric acid, while nitro-sulphuric acid, at low temperatures, gives about 66 per cent. o-nitro-toluol.

On further nitrogenation of o- and p-nitro-toluol we obtain: [**2, 4**]-**dinitro-toluol**, m.p. 70°; [**2, 5**]-**dinitro-toluol**, m.p. 48°; and [**2, 4, 6**]-**trinitro-toluol**, m.p. 82° (B. **21**, 433; **22**, 2679).

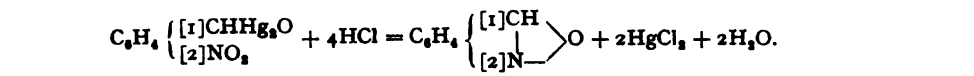
We must note the transformation of o-nitro-toluol into *anthranilic acid* by heating with an alkaline hydroxide, whereby o-nitroso-benzyl

alcohol and anthranile have been isolated as intermediate products (C. 1908, II. 210). The reaction passes through the following phases :



Similarly, we obtain from o-nitro-toluol-sulpho-acid *anthranile sulpho-acid* (C. 1903, I. 371), and, by heating o-nitro-toluol with Br to 170°, *dibromo-anthranilic acid.*

On boiling with HgO in an alkaline solution, o-nitro-toluol yields a mono- and a di-mercuric compound. The latter probably has the formula $NO_2[1]C_6H_4[2]CH\langle^{Hg}_{Hg}\rangle O$. It forms dark-yellow crystals, which decompose above 220°, and may be smoothly split up in the cold by means of concentrated HCl into $HgCl_2$ and *anthranile* (*q.v.*) (B. **40,** 4209 ; C. 1908, I. 1346) :



p-Nitro- and 2, 4-dinitro-toluol also react with HgO.

[1, 3]-, m-Nitro-toluol $CH_3[1]C_6H_4[3]NO_2$, m.p. 16°, b.p. 230°, is formed on nitrogenating aceto-p-toluidin and replacing the amido-group by hydrogen (B. **22,** 831). On further nitrogenation of m-nitro-toluol we obtain **[3, 4]-dinitro-toluol,** m.p. 61°, and **[3, 5]-dinitro-toluol,** m.p. 92° (B. **27,** 2209).

Nitro-Products of Alkyl-Benzols.

On account of the facility with which the aromatic nitro-compounds are produced, many of them are suitable for determining their fundamental hydrocarbons. Some of them may here be enumerated :

[4]-Nitro-o-xylol $NO_2[4]C_6H_3[1, 2](CH_3)_2$, m.p. 29° (B. **17,** 160 ; **18,** 2670). **[4, 5]-** and **[4, 6]-Dinitro-o-xylol,** m.p. 116° and 76° (**B. 35,** 628).

[5]-Nitro-m-xylol, m.p. 74°. **[2, 4]-Dinitro-m-xylol,** m.p. 82°. **[2, 6]-Dinitro-m-xylol,** m.p. 93°. **[2, 4, 6]-Trinitro-m-xylol,** m.p. 182° (B. **17,** 2424). **[4, 5, 6]-Trinitro-m-xylol,** m.p. 125° (C. 1906, II. 29 ; 1909, I. 1320).

[2]-Nitro-p-xylol, b.p. 239° (B. **18,** 2680). **[2, 6]-Dinitro-p-xylol,** m.p. 123°, and **[2, 3]-Dinitro-p-xylol,** m.p. 93°, form a double compound of m.p. 99° (B. **15,** 2304). **[2, 3, 6]-Trinitro-p-xylol,** m.p. 137° (B. **19,** 145).

[2, 4]-Dinitro-ethyl-benzol, $b.p._{10}$ 163°. **[2, 4, 6]-Trinitro-ethyl-benzol,** m.p. 37° (B. **42,** 2633).

Nitro-mesitylene $NO_2[2]C_6H_2[1, 3, 5](CH_3)_3$, m.p. 44° (B. **33,** 3625). **Dinitro-mesitylene,** m.p. 86°. **Trinitro-mesitylene,** m.p. 232° (B. **29,** 2201).

Nitro-pseudocumol $NO_2[5]C_6H_2[1, 2, 4](CH_3)_3$, m.p. 71°. **Dinitro-pseudocumol** $(NO_2)_2[3, 5]C_6H[1, 2, 4](CH_3)_3$, m.p. 172°. **[3, 5, 6]-Trinitro-pseudocumol** $(NO_2)_3[3, 5, 6]C_6[1, 2, 4](CH_3)_3$, m.p. 185° (B. **42,** 3608).

[4, 5, 6]-Trinitro-v-trimethyl-benzol $(NO_2)_3[4, 5, 6]C_6[1, 2, 3](CH_3)_3$, m.p. 209° (B. **19,** 2517).

Nitro-prehnitol $NO_2[5]C_6H[1, 2, 3, 4](CH_3)_4$, m.p. 61° (B. **21,** 905). **Dinitro-prehnitol,** m.p. 178°. **Dinitro-isodurol** $(NO_2)_2[4, 6]C_6[1, 2, 3, 5](CH_3)_4$, m.p. 156°. **Dinitro-durol** $(NO_2)_2[3, 6]C_6[1, 2, 4, 5](CH_3)_4$, m.p. 205°.

Nitro-pentamethyl-benzol, m.p. 154° (B. **42,** 4162).

[2, 4, 6]-Trinitro-ψ-butyl-toluol $(NO_2)_3[2, 4, 6]C_6H[1]CH_3[3]C(CH_3)_3$, m.p. 96°-97°, smells intensely of musk, and is marketed as "artificial musk" (B. **24,** 2832).

Nitro-Halogen Derivatives of the Alkyl-Benzols.

A large number of such compounds have been prepared.

2-Chloro-5-nitro-toluol, m.p. 44°, and **4-chloro-2-nitro-toluol,** m.p. 38°, by nitrogenation of o- and p-chloro-toluol respectively (B. **19,** 2438; **20,** 199). **3-Chloro-4-nitro-toluol,** m.p. 55°, from nitro-m-toluidin. For further halogen-nitro-toluols, see B. **37,** 1018.

2, 4, 6-Trinitro-5-chloro-toluol, m.p. 148°, is formed, besides the 2, 4-dinitro-compound, on nitrogenation of m-chloro-toluol. It is a homologue of picryl chloride. Here also the halogen is exceedingly reactive, and exchangeable for numerous other groups.

Nitro-bromo-durol, m.p. 178°, by nitrogenation of bromo-durol with nitro-sulphuric acid in chloroform solution. Very peculiar is the action of fuming nitric acid upon bromo-durol, leading to dinitro-durylic bromide, with displacement of the bromine atom and oxidation:

$$H\frac{CH_3\ CH_3}{CH_3\ CH_3}Br \longrightarrow NO_2\frac{CH_2\ COBr}{CH_3\ CH_3}NO_2.$$

Rules of Substitution.

Formation of Di-derivatives.—Chlorination and bromination of benzene and toluol, nitrogenation of monohalogen benzols and of toluol, give rise almost entirely to p- and o-di-derivatives, while nitrogenation of benzene produces chiefly m-dinitro-benzol. Phenol and aniline behave like toluol: p- and o-di-derivatives are mainly formed. On the other hand, benzol sulpho-acid $C_6H_5SO_3H$, benzoic acid C_6H_5COOH, benzaldehyde C_6H_5CHO, benzo-nitrile C_6H_5CN, aceto-phenone $C_6H_5CO.CH_3$, and a few other compounds, with so-called side groups, form mostly m-combinations. The substituents contained in the mono-derivatives therefore determine the place of further substitution. And it is not immaterial in what succession the substituents are introduced. Nitrogenation of chloro-benzol yields chiefly p-nitro-chloro-benzol, while chlorination of nitro-benzol produces mainly m-nitro-chloro-benzol.

Concerning the dependence of substitution processes upon atomic, and radicle, magnitudes of the substituents, see B. **23,** 130.

The following rule is given by Crum Brown and J. Gibson:—If the hydrogen link of the atom or radicle attached to the benzene nucleus in the mono-derivative cannot be oxidised *direct, i.e.* in one operation, to the corresponding hydroxyl compound, a further substitution gives o- and p-derivatives, otherwise m-derivatives (B. **25,** R. 672).

The following rule attempts an explanation of the various regularities of substitution. The second substituent enters the o- or p-position when the first substituent is attached, with much valence

energy, to the benzol-hydrocarbon atom, since there is then a greater amount of surplus energy attached to the C atom; when the first substituent is loosely bound, the m-position has more surplus energy, and the substitution will take place there (*J. pr. Ch.* 2, **66**, 321; cp. C. 1906, I. 458).

Formation of Tri-derivatives.—On further substitution (chlorination, nitrogenation) of the ortho- and para-di-derivatives, the substituent groups enter the para- and ortho-positions respectively, so that the di-derivatives [1, 2], and [1, 4] become tri-derivatives [1, 2, 4] (A. **192**, 219). From the meta-di-derivatives [1, 3] the [1, 3, 4] and [1, 2, 3]-tri-derivatives are obtained. If both substituent groups are of strongly acid character, as in m-dinitro-benzol [1, 3, 5]-derivatives are formed.

Formation of Tetra-derivatives.—If further substitution takes place in an unsymmetrical tri-derivative [1, 2, 4], unsymmetrical tetra-derivatives [1, 2, 4, 6] are usually produced. Aniline, phenol, etc., become trichloro- or trinitro-derivatives, in which the entering groups are in the *meta*-position [2, 4, 6]=[1, 3, 5] with respect to each other. If from these the groups OH and NH_2 are eliminated, symmetrical tri-derivatives $C_6H_3X_3$ [1, 3, 5] are obtained.

2. Nitroso-Derivatives of Benzene and the Alkyl-Benzols.

Mononitroso-derivatives of benzene hydrocarbons cannot be obtained from the benzols by substitution. They are produced: (1) by oxidation of the corresponding β-hydroxylamine derivatives with K bichromate and sulphuric acid, ferric chloride, or atmospheric oxygen:

$$C_6H_5NHOH+O=C_6H_5NO+H_2O;$$

(2) from anilines by oxidation with sulpho-mono-per-acid (B. **32**, 1675); (3) by electrolytic reduction of nitro-benzol without a membrane, using neutral electrolytes, *e.g.* solutions of Na, Mg, or Al sulphate. The formation of nitroso-benzol seems, in this case, to be secondary, the primary β-phenyl-hydroxylamine formed at the cathode being oxidised to nitroso-benzol at the anode (C. 1908, I. 911). The nitroso-compounds form colourless crystals of great volatility, coloured green, when melted or dissolved. This change of colour is probably due to the fact that the molecules, dimeric in the solid state, become dissociated into simple molecules on melting or dissolving (B. **34**, 3877). By oxidation the nitroso-benzols give nitro-bodies; by reduction, amido-bodies. With aromatic amines they condense to azo-bodies with elimination of water; with β-phenyl-hydroxylamines, to azoxy-bodies; with hydroxylamine, to so-called isodiazo-benzols; with phenyl-hydrazine, to diazo-oxy-amido-compounds; with the salts of nitro-hydroxylaminic acid (Vol. I.), or benzol-sulpho-hydroxamic acid, they form β-phenyl-nitroso-hydroxylamines (Bamberger, B. **28**, 245, 1218; **29**, 102; **32**, 3554; C. 1904, I. 24):

$$C_6H_5NO+NH_2.C_6H_5 = C_6H_5N:N.C_6H_5+H_2O$$

$$C_6H_5NO+NH(OH).C_6H_5 = C_6H_5N\underset{O}{\diagdown\!\diagup}NC_6H_5+H_2O$$

$$C_6H_5NO+NH_2.OH = C_6H_5N:N.OH+H_2O$$

$$C_6H_5NO+NH_2.NHC_6H_5 = C_6H_5N(OH)N:NC_6H_5(+2H)$$

$$C_6H_5NO+HON:NO_2Na = C_6H_5N(OH)NO+NO_2Na.$$

With substances containing CH_2 groups which have become reactive through the vicinity of acid-forming radicles, the nitroso-benzols yield ketone-aniles with elimination of water, *e.g.*

$$C_6H_5NO+CH_2\begin{matrix}CN\\C_6H_5\end{matrix}=C_6H_5N:C\begin{matrix}CN\\C_6H_5\end{matrix}+H_2O$$

(B. **34**, 494). By concentrated H_2SO_4 the nitroso-benzols are polymerised like aldol, forming p-nitroso-diphenyl-hydroxylamines $NOC_6H_4N(OH)C_6H_5$ (B. **31**, 1513; **32**, 219). Nitroso-benzol in these reactions strikingly resembles the aldehydes, especially benzaldehyde C_6H_5CHO (*q.v.*), from which it is distinguished by the CH group being replaced by a nitrogen atom. With diazo-methane (Vol. I.) the nitroso-benzols form addition products, which give off N, and pass into the N-phenyl-ether of glyoxime (B. **30**, 2791).

Nitroso-Benzol C_6H_5NO, m.p. 68°, first obtained in solution by the action of nitrosyl bromide upon mercury diphenyl (v. Baeyer, 1874). Now prepared by oxidation of β-phenyl-hydroxylamine or aniline, or by electrolytic reduction of nitro-benzol. Produced in small quantities with other bodies by oxidation of diazo-benzol chloride; also from diazo-benzol perbromide with alkalies, and by distillation of azoxy-benzol (B. **27**, 1182, 1273). Illumination completely decomposes nitroso-benzol in benzene solution: besides some resins, azoxy-benzol, nitro-benzol, aniline, and o-oxyazo-benzol are formed (B. **35**, 1606).

o-, m-, p-Nitroso-toluol $CH_3.C_6H_4.NO$, m.p. 72°, 53°, 48°. **2, 3-, 2, 4-, 2, 5-, 2, 6-,** and **3, 4-Nitroso-xylol** $(CH_3)_2C_6H_3NO$ melt at 91°, 41°, 101°, 141°, and 45°. **Nitroso-mesitylene** $(CH_3)_3[2, 4, 6]C_6H_2NO$, m.p. 122°, best obtained from amido-mesitylene (mesidin) with sulpho-mono-per-acid (A. **316**, 257, etc.). **p-Chloro-** and **p-Bromo-nitro-benzol**, m.p. 87° and 92°.

o-, m-, and **p-Nitro-nitroso-benzol,** m.p. 126°, 90°, and 119°, by oxidation of the three nitranilines with sulpho-mono-per-acid (B. **36**, 3803; **38**, 4011). o- and p-Nitro-nitroso-benzol are also obtained by reduction of o- and p-dinitro-benzol by hydroxylamine and stannous oxide, in strongly alkaline methyl-alcoholic solution. This at first gives strongly coloured alkali salts of a dinitronic acid resembling quinone, $C_6H_4\begin{matrix}NOOK\\NOOK\end{matrix}$, from which acidulation liberates water and produces the nitro-nitroso-benzols. Similarly, o-nitro-nitroso-p-xylol, m.p. 130·5°, from o-dinitro-p-xylol. m-Dinitro-benzol is not reduced under similar conditions, but undergoes substitution with formation of dinitro-amido-compounds (B. **39**, 2526, 2533).

Trinitro-nitroso-benzol $(NO_2)_3[2, 4, 6]$-C_6H_2NO, m.p. 198° (B. **34**, 59).

2-Nitro-6-nitroso-toluol, m.p. 117°, **2-Nitro-4-nitroso-toluol,** m.p. 87° (B. **40**, 3331).

p-Dinitroso-derivatives are formed by oxidation of p-quinone di-oximes in alkaline solution with potassium ferricyanide, *e.g.* **p-Dinitroso-toluol** $CH_3[1]C_6H_3[2, 5](NO)_2$, m.p. 133°, from tolu-quinone dioxime $CH_3C_6H_3(NOH)_2$, yellow needles with a suffocating odour of quinone, converted by fuming nitric acid into p-dinitro-toluol, and by hydroxylamine chloride into tolu-quinone dioxime (B. **21**, 734, 3319).

o-Dinitroso-derivatives are obtained from o-nitro-diazo-imides, by heating, and elimination of N.

o-Dinitroso-benzol $C_6H_4[1,2](NO)_2$, m.p. 72°, from o-nitro-diazo-benzol-imide at 90°, yields on reduction o-quinone dioxime (A. **307,** 28).

m-Dinitroso-benzol $C_6H_4[1,3](NO)_2$, m.p. 146·5°, formed, besides m-nitro-nitroso-benzol, during reduction of m-dinitro-benzol, with zinc dust, and glacial acetic acid in alcoholic solution (B. **38,** 1899).

1, 2, 3, 4-Tetranitroso-benzol $C_6H_2(NO)_4$, m.p. 93°, from diquinoyl-tetroxime by oxidation with sodium hypochlorite (B. **32,** 505).

Dinitro-dinitroso-benzol $C_6H_2(NO_2)_2(NO)_2$, m.p. 133°, golden flakes, from picryl chloride with hydroxylamine in acetic solution. By oxidation it yields *as*-tetranitro-benzol (B. **34,** 55).

3. β-Alphyl- or Aryl-Hydroxylamines.*

These very reactive substances are obtained as intermediate products in the reduction of nitro- and nitroso-benzols. They are very sensitive to alkalies and acids, and they are therefore prepared by means of neutral reducing agents, as by the action of zinc dust, and sal ammoniac solution, upon nitro-benzols, or of Al amalgam and water on the etheric solutions of nitro-benzols (B. **29,** 494, 863, 2307).

Particularly straightforward is the electrolytic reduction of the nitro-compounds in acetic solution with Na acetate (B. **38,** 3076). With alcoholic ammonium sulphide it is easy to obtain β-aryl-hydroxylamine. Polynitro-compounds in this case yield nitro-aryl-hydroxylamines by partial reduction (B. **41,** 1936). Aniline is oxidised to β-phenyl-hydroxylamine by mono-sulpho-per-acid (B. **32,** 1675).

The aryl-hydroxylamines reduce ammoniacal silver solution and Fehling's solution. They energetically absorb atmospheric oxygen in aqueous solution, especially in the presence of alkali. Hydrogen peroxide is thus generated, and the hydroxylamines are first oxidised to nitroso-benzols, which, however, mostly combine with the unchanged aryl-hydroxylamine to azoxy-benzols :

$$C_6H_5NO + C_6H_5NHOH = C_6H_5N\overset{O}{\diagdown\diagup}NC_6H_5 + H_2O.$$

By *ortho-* and *para*-position methyl groups this reaction is retarded, and in mesityl-hydroxylamine it is entirely suspended (A. **316,** 257).

With diazo-benzol solutions the aryl-hydroxylamines yield diazo-oxy-amido-compounds, *e.g.* $C_6H_5N(OH)N_2C_6H_5$; this reaction is also hindered by o- and p-methyl groups.

Sulphuric acid transposes phenyl-hydroxylamine, and hydroxylamines in a free para-position, into p-amido-phenols :

$$C_6H_5NHOH \longrightarrow HO[4]C_6H_4[1]NH_2.$$

If the para-position is occupied by a methyl group, transposition occurs all the same ; but so-called "quinols" are produced with rejection of NH_3. These quinols are closely related to the *quinones* (*q.v.*), and may easily pass by further atomic displacement into methylated hydroquinones, *e.g.*

$$CH_3\text{-}\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}NHOH \longrightarrow \begin{matrix} HO \\ CH_3 \end{matrix}\diagdown\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{:}O \longrightarrow HO\text{-}\underset{CH_3}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}OH.$$

* "Alphenyl" is a contraction of "alkyl phenyl" $C_nH_{2n+1}C_6H_4$ (Bamberger). The word "aryl" = aromatic radicle has been lately proposed for these residues (Vorländer, *J. pr. Ch.* 2, **50,** 247).

Concentrated sulphuric acid transforms phenyl-hydroxylamine into p-amido-phenol-o-sulpho-acid. Concentrated nitric acid transforms m-tolyl-hydroxylamine into chloro-toluidines (B. **33**, 3600; **34**, 61; **35**, 3697). Cp. the similar transpositions of aromatic nitramines, nitrosamines, and chloramines, into p-nitro-, nitroso-, and chlor-aniline.

With aldehydes, *e.g.* benzaldehyde, the aryl-hydroxylamines reject water, and form n-aryl-ether from aldoximes, *e.g.* $C_6H_5N\!\!<\!\!\begin{matrix}\\O\end{matrix}\!\!>\!\!CHC_6H_5$ (C. 1905, II. 764). But formaldehyde gives methylene-diaryl-hydroxylamines, *e.g.* $CH_2[N(OH)C_6H_5]_2$. Methylene-diphenyl-hydroxylamine is easily converted into the n-phenyl-ether of glyoxime, but under the influence of anhydrous SO_4Cu it passes into diphenyl-oxy-formamidin $CH\!\!<\!\!\begin{matrix}N(OH)C_6H_5\\NC_6H_5\end{matrix}$.

Acid chlorides acidulate the aryl-hydroxylamines in their nitrogens, *e.g.* **N-Formyl-phenyl-hydroxylamine** $C_6H_5N(CHO)OH$, m.p. 71°; **N-Acetyl-phenyl-hydroxylamine** $C_6H_5N(COCH_3)OH$, m.p. 67°; **N-Benzol-sulphono-phenyl-hydroxylamine** $C_6H_5N(SO_2C_6H_5)OH$ (B. **34**, 243; **35**, 1883).

β-Phenyl-hydroxylamine C_6H_5NHOH, m.p. 81°. Chlorohydrate, white crystalline flakes, precipitated from ether. With metals it also forms salts: C_6H_5NHONa from phenyl-hydroxylamine with Na in ether.

To the above transpositions of β-phenyl-hydroxylamine we may add the formation of nitroso-phenyl-hydroxylamine with N_2O_3, and of phenyl-sulphaminic acid $C_6H_5NSO_3H$ with SO_2 (in etheric solution); in aqueous solution, phenyl-hydroxylamine, with SO_2, gives o-aniline-sulpho-acid (cp. B. **34**, 246). For the action of BrCN upon β-phenyl-hydroxylamine, see B. **37**, 1536.

o-, m-, p-Tolyl-hydroxylamine $CH_3C_6H_4NHOH$, m.p. 44°, 68°, 94°; **2, 3-, 2, 4-, 2, 5-, 2, 6,** and **3, 4-Xylyl-hydroxylamine** $(CH_3)_2C_6H_3.NHOH$, m.p. 74°, 64°, 91°, 98°, and 101°; **Mesityl-hydroxylamine** $(CH_3)_3[2, 4, 6]C_6H_2NHOH$, m.p. 116°.

β-Chloro-phenyl-hydroxylamine ClC_6H_4NHOH, m.p. 88°. **m-Nitro-phenyl-hydroxylamine** $NO_2C_6H_4NHOH$, m.p. 119°, by electrolytic reduction of m-dinitro-benzol (B. **38**, 3078). **3, 5-Dinitro-phenyl-hydroxylamine** $(NO_2)_2C_6H_3NHOH$, m.p. 135°–137°, from sym. trinitro-benzol by reduction with H_2S (C. 1905, II. 1330). **2, 4, 6-Trinitro-phenyl-hydroxylamine** $(NO_2)_3C_6H_2NHOH$, m.p. 174°, from picryl chloride with hydroxylamine chlorohydrate. On heating with caustic soda it passes into an iso-picric acid, isomeric with picric acid (B. **34**, 57).

Diphenyl-hydroxylamine $(C_6H_5)_2NOH$ has not up to the present been isolated; but it probably forms the first product of the splitting of tetraphenyl-hydrazin (*q.v.*) with concentrated acids (B. **41**, 3482).

o, p-Dinitro-diphenyl-hydroxylamine $(NO_2)_2[2, 4]C_6H_3N(OH)C_6H_5$, m.p. 114° with decomposition, orange-coloured needles, from 1, 2, 4-bromo-nitro-benzol and β-phenyl-hydroxylamine. Also formed on treating tetranitro-tetraphenyl-hydrazin with concentrated sulphuric acid. With alkalies, it forms salts, of a brownish-red colour, which, perhaps, belong to the quinoid type:

$$C_6H_5\!\!<\!\!\begin{matrix}O\\\\N\end{matrix}\!\!=\!\!\begin{matrix}NO_2 & H\\H & H\end{matrix}\!\!=NOOK.$$

In concentrated SO_4H_2 it dissolves without change, with an intense violet colour (B. **39**, 3038).

p-Nitroso-diphenyl-hydroxylamine $NOC_6H_4N(OH)C_6H_5$, shiny bronze scales, melting at 147°–152° with active decomposition, produced by action of concentrated SO_4H_2 upon nitroso-benzol. The deep-red salts, and the *methyl ester* derived from them (m.p. 138°), may be referred to the quinoid form $HON:C_6H_4:NOC_6H_5$. By boiling with dilute SO_4H_2 or NaOH it is split back into nitroso-benzol (B. **39**, 3036).

4. β-Alphyl-Nitroso-Hydroxylamines.

β-Phenyl-nitroso-hydroxylamine $C_6H_5N(OH).NO$ or $C_6H_5NO(:NOH)$, m.p. 59°, produced

(1) From ice-cold hydrochloric β-phenyl-hydroxylamine solution with solution of Na nitrite;

(2) By action of hydroxylamine and Na alcoholate upon nitro-benzol (C. 1899, II. 371);

(3) From nitroso-acet-anilide, or from potassium-n-diazo-benzol by oxidation with alkaline H peroxide solution (B. **42**, 3568, 3582);

(4) By conducting nitric oxide into an etheric solution of phenyl-magnesium bromide (A. **329**, 190);

(5) By transposition of nitroso-benzol with the Na salts of nitro-hydroxylaminic acid $HON:NO_2H$ (Vol. I. 194) or benzol-sulphydroxamic acid (C. 1904, I. 24). Ammonium salt, m.p. 164°. The slightly soluble iron salt is characteristic. β-Phenyl-nitroso-hydroxylamine is a very unstable body, decomposing spontaneously into nitroso-benzol, diazo-benzol nitrate, and other substances, such as p_2-dinitro-diphenylamine $NH(C_6H_4NO_2)_2$. By methylating its salts with methyl iodide, or the free substance with diazo-methane, a *methyl ether*, m.p. 38°, is generated, probably referable to the tautomeric form $C_6H_5NO(:NOH)$, since reduction with Al amalgam transforms it into diazo-benzol-methyl ester $C_6H_5N:NOCH_3$ (B. **31**, 574).

p-Chloro- and **p-Bromo-β-phenyl-nitroso-hydroxylamine**, m.p. 74·5° and 87°.

5. Amido-Derivatives or Anilines.

The aromatic amido-compounds are derivable from benzene, and the alkyl-benzols, by replacing hydrogen by amido-groups:

$C_6H_5.NH_2$	$C_6H_4(NH_2)_2$	$C_6H_3(NH_2)_3$
Aniline, amido-benzol	Diamido-benzol	Triamido-benzol.

On the other hand, we may regard them as derivatives of ammonia, which indicates the existence of primary, secondary, and tertiary amines of the benzene series:

$C_6H_5.NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
Phenylamine	Diphenylamine	Triphenylamine

$C_6H_5NHCH_3$	$C_6H_5N(CH_3)_2$
Phenyl-methylamine	Phenyl-dimethylamine.

If, on the other hand, the hydrogen in the side chains of the benzene homologues is replaced by the amido-group, the true analogues of the

fatty amines are produced, like $C_6H_5.CH_2.NH_2$ benzylamine, and these are considered in connection with the corresponding alcohols.

A. Primary Phenylamines.

Formation of the primary phenylamines, in which the amido-groups are joined to the benzene nucleus.

Reduction Reactions.

1. The amido-derivatives are prepared almost exclusively by reduction of the corresponding nitro-compounds :

$$C_6H_5NO_2+6H=C_6H_5NH_2+2H_2O.$$

As intermediate products of the reduction, some conditions yield the β-phenyl-hydroxylamines and nitroso-benzols.

The most important methods of reduction are :

(*a*) Action of ammonium sulphide in alcoholic solution (Zinin, 1842) :

$$C_6H_5.NO_2+3H_2S=C_6H_5.NH_2+2H_2O+3S.$$

In the polynitro-compounds only one nitro-group is easily reduced in this way, and nitro-amido-compounds are produced.

In the chloro-nitro-benzols the nitro-group is only reduced by Am_2S if it is not in the neighbourhood of chlorine, or of another nitro-group ; otherwise chlorine, or another nitro-group, is replaced by sulphur or SH (B. **11**, 1156, 2056). Generally speaking nitro-groups in *ortho* position with reference to other substituents are not reducible by Am_2S, but the reduction can usually be brought about by stannous chloride (B. **35**, 2073 ; C. 1905, II. 1330, but cp. C. 1902, I. 115). On the reduction of nitro-compounds with fixed sulphur alkalies, see C. 1903, I. 746 ; 1907, I. 404.

(*b*) Action of zinc and HCl upon alcoholic solutions of nitro-bodies (A. W. Hofmann) ; action of iron filings and acetic or hydrochloric acid. Iron and HCl are used industrially for producing aniline, and o- and p-toluidin.

(*c*) Action of tin and HCl or acetic acid (B. **15**, 2105) ; or a solution of stannous chloride in HCl :

$$C_6H_5NO_2+3Sn \quad +6HCl=C_6H_5NH_2+3SnCl_2+2H_2O$$
$$C_6H_5NO_2+3SnCl_2+6HCl=C_6H_5NH_2+3SnCl_4+2H_2O.$$

The last reaction may serve for the quantitative determination of the nitro-groups. By adding to the alcoholic solution of a polynitro-compound, an alcoholic hydrochloric solution of the calculated amount of $SnCl_2$, one is able to obtain a step-by-step reduction. In the case of o- p-, [2, 4]-dinitro-toluol the [4]-NO_2 group is thus reduced, while with alcoholic Am_2S the [2]-NO_2 group is reduced (B. **19**, 2161 ; cp. B. **35**, 2073). In the reduction with Sn and HCl an addition of graphite favours the reaction (*J. pr. Ch.* 2, **65**, 579). On the speed of reaction with $SnCl_2$ and HCl, see *Z. phys. Ch.* **56**, 1.

(*d*) Electrolytic reduction in mineral acid solution converts nitro-compounds into amido-compounds. In concentrated H_2SO_4 solution the chief product is p-amido-phenol, generated by transposition of the

β-phenyl-hydroxylamine first formed. For a summary of literature, see A. **855**, 175.

In many cases the following reducing agents have been used with advantage:

(*e*) Titanium trichloride, and HCl, especially for quantitative determinations of the nitro-groups (B. **36**, 1554).

(*f*) Sodium arseniate (*J. pr. Ch.* 2, **50**, 563).

(*g*) Zinc dust in alcoholic, or ammoniacal, solution.

(*h*) Ferric sulphate with baryta water (B. **24**, 3193), or ammonia (B. **15**, 2294), for reducing nitro-bodies soluble in water or alkalies.

(*i*) Molecular hydrogen reduces nitro-bodies smoothly to anilines, if the former are conducted at higher temperatures (200°–400°) over finely divided metals, such as copper, nickel, etc. (C. 1901, II. 681); or if in the presence of colloid metals, especially palladium and platinum at ordinary temperatures, they are treated with hydrogen in alcoholic, or etheric, solution (B. **40**, 2209).

2. By reduction of nitroso-compounds; see Nitroso-benzol and Nitroso-dimethyl-aniline.

3. By reduction of hydrazo-compounds, and hydrazins (*q.v.*).

Exchange Reactions.

4. By replacing a halogen atom or nitro-group, an hydroxyl or an alkoxyl group, by an amido-group, the halogen benzols, heated by themselves in ammonia, only yield traces of amido-compounds. But the transformation is readily effected in the presence of small quantities of copper salts (C. 1909, I. 475). The reaction is the readier without a catalyser the more nitro-groups are also introduced. [1, 2]-Chloro-benzol, bromo-nitro-benzol, [1, 2]-dinitro-benzol, [1, 2]-nitro-phenol and its alkyl ethers, [1, 4]-chloro- and bromo-nitro-benzol, [1, 4]-nitro-phenol and its alkyl ethers, when heated with ammonia, give nitro-amido-compounds. The [1, 3]- or *meta*-compounds do not react (B. **21**, 1541; A. **174**, 276).

Phenols can be directly converted into primary (and secondary) amines, by heating with $ZnCl_2.NH_3$ to 300°–350° (B. **16**, 2812; **17**, 2635; **19**, 2916; **20**, 1254). An easier reaction than that of the phenols is shown by the naphthols:

$$\underset{\text{Naphthol}}{C_{10}H_7.OH} + NH_3 \xrightarrow{ZnCl_2} \underset{\text{Naphthylamine.}}{C_{10}H_7NH_2} + H_2O$$

5. By heating the halogen derivatives and the alkaline sulphonates with Na amide, $NaNH_2$ (B. **39**, 3006).

6. A replacement of the carboxyl group of aromatic carboxylic acids by the amine group may be brought about through the intermediary of (*a*) the amides, (*b*) the azides, of these acids as in the aliphatic carboxylic acids (Hofmann, Curtius). To this may be added (*c*) Beckmann's transformation of the oximes of aromatic ketones into acidulated aromatic amines (Vol. I.), from which the amines are obtained by saponification:

$$C_6H_5C(NOH)CH_3 \longrightarrow C_6H_5NH.COCH_3 \longrightarrow C_6H_5NH_2.$$

7. A direct introduction of the amido-group into benzene hydro-

carbons may be effected by heating the latter with hydroxylamine chlorohydrate, and Al or Fe chloride (B. **34**, 1778):

$$C_6H_6+NH_2OH \xrightarrow{Al_2Cl_6} C_6H_5NH_2+H_2O.$$

But this only gives a small amount of anilines.

III. Separation Reactions.

8. By heating amido-carboxylic acids:

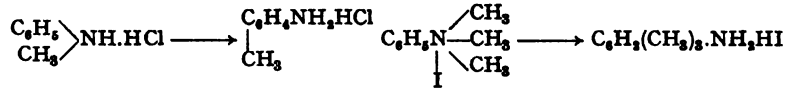
$$\underset{\text{Diamido-benzoic acids}}{(NH_2)_2C_6H_3CO_2H} = CO_2 + \underset{\text{Phenylene-diamine.}}{C_6H_4(NH_2)_2}$$

9. By heating secondary, and tertiary, amines with HCl, and from the quaternary Am salts, by quick heating, without additions:

$$C_6H_5.NHCH_3+HCl=C_6H_5.NH_2+CH_3Cl$$
$$C_6H_5.NHC_2H_5.HBr=C_6H_5.NH_2+C_2H_5Br.$$

IV. Nuclear Syntheses.

10. On heating aniline with methyl chloride, monomethyl-aniline chloride is first formed, and, at higher temperatures, this splits again into methyl chloride and aniline; at 340° methyl chloride brings about the replacement of nuclear H in aniline by methyl, thus producing toluidin chlorohydrate. Phenyl-trimethyl-ammonium iodide gives mesidine iodo-hydrate:



Phenyl-methylamine chlorohydrate — Toluidin chlorohydrate — Phenyl-trimethyl-ammonium iodide — Mesidin-iodo-hydrate.

In this way secondary, and tertiary, aromatic bases may be converted into isomeric primary ones. Instead of the halogen salts of the secondary, and tertiary, bases, one can also heat the salts of primary bases with suitable alcohols to 300° (B. **18**, 1729):

$$\underset{\text{Aniline chlorohydrate}}{C_6H_5NH_2HCl} + \underset{\text{Isobutyl-alk.}}{C_4H_9OH} = \underset{\text{Amido-tertiary-butyl-benzol.}}{C_4H_9.C_6H_4NH_2.HCl} + H_2O$$

Or free bases are heated with paraffin alcohols, and zinc chloride, to 250° (B. **16**, 105).

11. The oximes of many hydro-aromatic ketones, such as those of methyl- and dimethyl-cyclo-hexenone, trimethyl-cyclo-hexenone, or iso-aceto-phenone, yield primary anilines on heating with HCl, with atomic displacement (A. **322**, 379).

PROPERTIES AND TRANSFORMATIONS OF PHENYLAMINES.

The primary amines are colourless compounds of a peculiar, and not unpleasant, odour, and can be distilled, without decomposition, at ordinary pressures. As regards formation of salts they resemble alkylamines (Vol. I.), but they are much feebler bases than the primary alkylamines, have no alkaline reaction, and are but slightly soluble in water, though volatile with water vapour.

The basic character of primary phenylamines is further weakened by the entry of negative groups ; the salts of the di-substituted anilines, such as $C_6H_3Cl_2.NH_2$ and $C_6H_3(NO_2)_2.NH_2$, are decomposed by water alone, and cannot survive. The compounds resemble the carboxylic amides in chemical behaviour, just as the corresponding oxy-compounds, or phenols, have the character of acids.

Hydrogen reduces the amido-compounds to the corresponding hexahydro-anilines, on leading their vapours over finely divided nickel, at 190°, or on heating at high pressure in presence of nickel. The resulting bodies again show, as cyclo-alkylamines, the strongly basic character of the aliphatic amines.

Aniline will be studied in detail as the type of primary phenylamines. But first the following general reactions of the amido-group will be specified :

1. Alkali metals dissolve on heating, with liberation of H. From aniline we obtain potassium anilide C_6H_5NHK, and dipotassium anilide $C_6H_5NK_2$.

2. Halogen alkyls combine with the anilines to secondary, tertiary, and finally to quaternary ammonium compounds (Vol. I.).

3. One molecule of an aldehyde combines with one or two molecules of a primary amine, with liberation of water (B. **25**, 2020). With furfurol all primary anilines give intensely red compounds.

4. Of extreme importance, for the development of aromatic chemistry, has been the behaviour of free primary anilines, and their salts, with nitrous acid. Diazo-amido- and diazo-compounds are produced, the latter forming the links in the conversion of nitro- and amido-compounds, into the most diverse substitution products.

5. With thionyl chloride the primary anilines behave like the primary aliphatic amines (Vol. I.) ; thionyl-anilines are thus produced.

6. A hydrogen atom of the amido-group is very easily replaced by acid residues, acid anilides being thus formed, which correspond to the acid amides (Vol. I.). The easily crystallised acetic compounds are formed with special frequency.

7. Like the primary aliphatic amines (Vol. I.), the primary anilines give, with chloroform, and alkaline hydroxides, carbyl-amines.

8. With CS_2 the primary anilines combine to di-aryl-sulpho-uric compounds, with liberation of SH_2, while the primary aliphatic amines yield ammonium alkyl-dithio-carbaminates (Vol. I.).

9. Of significance for the development of quinolin chemistry has been the synthesis of quinolin (*q.v.*), and other bases containing quinolin nuclei, on heating aniline, and other primary aromatic bases, with glycerin, sulphuric acid, and nitro-benzol. Quinolin derivatives are also produced by condensation into fatty aldehydes by HCl or H_2SO_4.

10. Primary aromatic bases, heated with α-halogen-keto-compounds, yield indols (*q.v.*), sometimes with dihydro-pyrazin derivatives (*q.v.*).

ANILINE, *phenylamine* [*aminophene*] [*amino-benzene*) $C_6H_5NH_2$, m.p. −8°, b.p. 184°, D_0 1·0361, is an oil of a feebly aromatic odour, soluble at 12·5°, in 31 parts water (B. **10**, 709).

Historical.—Aniline was first discovered in 1826, by Unverdorben, during distillation of indigo, and was called " crystalline " on account

of the crystallising power of its salts. In 1834 Runge found it in coal-tar, and called it "cyanol," on account of its blue colour in bleaching-powder solution. In 1841 Fritzsche prepared a base, by distillation of indigo with KHO, and called it "aniline" from the name of the indigo plant, *Indigofera anil*. In the same year Zinin prepared "benzidame" by reducing nitro-benzol with Am_2S. The identity of the four bases was proved by A. W. Hofmann in 1843 (A. **47**, 37).

Industrially, aniline is obtained on a large scale by reduction of nitro-benzol with iron, and about one-fortieth of the HCl required according to the equation:

$$C_6H_5NO_2+2Fe+6HCl=C_6H_5NH_2+Fe_2Cl_6+2H_2O.$$

Probably only $FeCl_2$ is formed at first, and its presence brings about a reduction of the nitro-benzol by iron and water, the ferrous chloride serving as a carrier. The finely divided moist metal is the immediate reducing agent (B. **27**, 1436, 1815).

$$C_6H_5NO_2+3Fe+6HCl=C_6H_5NH_2+3FeCl_2+2H_2O$$
$$C_6H_5NO_2+2Fe+4H_2O=C_6H_5NH_2+Fe_2OH)_6.$$

The other means which can be used for reducing nitro-benzol to aniline have been explained above, where aniline has been usually chosen as the primary phenylamine. The same applies to the other reactions. Aniline is almost as much used in reactions as ammonia, and is the generator in numerous aromatic compounds. In spite of its feeble basicity, it precipitates zinc, aluminium, and ferrous salts, and displaces ammonia from its salts on account of being less volatile.

Aniline is a poison. It is a solvent for many bodies, *e.g.* indigo.

Aniline is very sensitive to oxidisers. It gradually colours brown in air, and becomes resinous. Bleaching-powder solution colours aniline purple-violet (B. **27**, 3263). With sulphuric acid, and a few drops of potassium bichromate, aniline colours red, and, afterwards, an intense blue. On oxidising aniline with hot chloride of lime, or with cold MnO_4K, it can be reconverted into nitro-benzol, through a series of intermediate products (B. **26**, 496; **31**, 1522). With chromic acid it yields *quinone* (*q.v.*); with chlorides, in the presence of certain metallic salts, it gives *aniline black* (*q.v*).

With nitroso-benzol aniline combines to azo-benzol, and with caustic potash and nitro-benzol it gives azo-benzol, and *phenazin oxide* (B. **84**, 2442).

Aniline is used in preparing numerous dyes and medicines, such as *aniline black*, *fuchsin*, etc., and *antifebrin*, *antipyrin*, etc.

Aniline salts.—**Chlorohydrate** is obtained quite pure and dry by conducting HCl through an etheric aniline solution, m.p. 198°, b.p. 245° (B. **31**, 1698); industrially it is called "aniline salt." In water it rapidly dissolves. **Platinum chloride double salt,** yellow needles, from alcohol. **Stannous** and **stannic chloride double salt** $SnCl_2.2C_6H_5.NH_2.HCl+2H_2O$ and $SnCl_4.2C_6H_5.NH_2.HCl+2H_2O$. **Sulphate** $(C_6H_5NH_2)_2SO_4H_2$. **Thiosulphate** $S_2O_3H_2(C_6H_5NH_2)_2$: only primary anilines form normal thiosulphates, not secondary or tertiary ones (C. 1902, I. 303). *Nitrate* forms rhombic plates; *oxalate*, rhombic prisms. Not only the chlorohydrate but also free aniline forms double

salts with some salts. It also combines additively with trinitro-benzol.

Potassium anilide: C_6H_5NHK and $C_6H_5NK_2$ are unknown in a pure condition. The formation of di- and trimethylamine, by action of bromo-benzol upon the reaction product of K upon aniline, proves that the hydrogen of the amido-group is replaced by K. Na does not act upon aniline below 200°. Small quantities of Cu, CuO, etc., facilitate the formation of the Na salt (C. 1909, II. 1512). Cp. also acetanilide, and monomethyl-aniline.

Magnesium haloid compounds of aniline (like C_6H_5NHMgI) are obtained in the shape of crystalline precipitates by the action of aniline upon an etheric solution of alkyl-magnesium haloids (C. 1903, I. 1024):

$$C_6H_5NH_2+CH_3MgI=C_6H_5NH.MgI+CH_4.$$

They strongly absorb CO_2, forming salts of carbaminic acid (B. **37,** 3978); with acid esters they give the corresponding acid anilides (C. 1904, I. 201; 1906, I. 1000).

Amido-methyl-benzols.—Some representatives of this group are of great importance in the dye industry, especially o- and p-toluidin. Most of the bases are liquid at ordinary temperatures, but easily yield acetic compounds, on boiling with glacial acetic acid, or treating with acetyl chloride or acetic anhydride. These substituted acetamides are easily crystallising bodies, of definite melting-point, very suitable for characterisation of the bases, from which they are easily obtained. The melting-point of the acetic compound is therefore, in what follows, added to the m.p. or b.p. of the base. Amido-methyl-benzols are obtained by the reduction of the corresponding nitro-compounds, and by heating chlorides of the bases, methylated as regards the nitrogen, like dimethyl-aniline $C_6H_5N(CH_3)_2$, under pressure, at high temperature.

Toluidin $CH_3.C_6H_4NH_2$.—The three toluidins are isomeric with benzyl-amine $C_6H_5CH_2NH_2$ (treated in connection with benzyl-alcohol) and with methyl-aniline $C_6H_5NHCH_3$. They are obtained by reduction of the three nitro-toluols. m-Toluidin is also prepared by reduction of m-nitro-benzol chloride, a transformation product of m-nitro-benzaldehyde (B. **15,** 2009; **18,** 3398). p-Toluidin was discovered in 1845 by A. W. Hofmann and Muspratt (A. **54,** 1).

o-Toluidin, liquid	b.p. 197°;	*Acet-o-toluide,* m.p. 110°,	b.p. 296°
m-Toluidin, ,,	,, 199°;	*Acet-m-toluide,* ,, 65°,	,, 303°
p-Toluidin, m.p. 45°	,, 198°;	*Acet-p-toluide,* ,, 153°,	,, 307°

p-Toluidin unites with one molecule of water to a monohydrate $CH_3C_6H_4.NH_2.H_2O$, m.p. 41·5°, which may be used for isolating, and purifying, the base (C. 1908, I. 2092).

The *chlorohydrates* of o-, m-, and p-toluidin melt at 215°, 228°, and 243° respectively, and boil without decomposition at 242°, 250°, and 257° respectively (B. **31,** 1698).

Separation of o- and p-toluidin.—Nitrogenation of toluol forms o- and p-nitro-toluol, from which the industrially important toluidins are obtained. The o-toluidin is separated from the p-toluidin by treating the mixed bases with an amount of sulphuric acid insufficient for

complete neutralisation, and distilling. The stronger p-base remains behind, as a sulphate. Or we can utilise the greater solubility of the o-toluidin oxalate (*J. pr. Ch.* 2, **14**, 449). Aniline, o- and p-toluidin may also be separated by the different behaviour of their chlorohydrates towards mono-sodium phosphate (B. **19**, 1718, 2728; cp. B. **29**, R. 434).

In the aniline dye industry there is a distinction between :

Aniline oil for blue: pure aniline.
Aniline oil for red: molecular quantities of aniline, o- and p-toluidin.
Aniline oil for safranin: aniline and o-toluidin, from the distillate of the fuchsin mixture.

The free toluidins are easily transformed, by oxidation, into azo-compounds (B. **26**, 2772). If the amido-group is protected from oxidation, by introducing an acid radicle, *e.g.* the acetyl group, the methyl group may be oxidised to a carboxyl group with potassium permanganate, and o-aceto-toluide may thus be converted into o-acetamido-benzoic acid (B. **14**, 263). In the chlorination, bromination, or nitrogenation of the aceto-toluides, the negative substituent is mostly placed in the o-position with respect to the acet-amido group (see Rules of Substitution).

o-Toluidin, like aniline, is coloured violet by chloride of lime solution and HCl, but p-toluidin is not. Iron chloride separates, from the hydrochloric o-toluidin solution, a blue body, known as toluidin blue.

Xylidins $(CH_3)_2C_6H_3NH_2$. All the six possible isomers are known :

v-o-Xylidin, liquid,	b.p. 223°;	corresponding	*Acetoxylide,*	m.p.	134°
as-o-Xylidin, m.p. 49°,	,, 226°;	,,	,,	,,	99°
v-m-Xylidin, liquid	,, 216°;	,,	,,	,,	170°
as-m-Xylidin ,,	,, 212°;	,,	,,	,,	120°
s-m-Xylidin ,,	,, 220°;	,,	,,	,,	144°
p-Xylidin, m.p. 15°	,, 213°;	,,	,,	,,	180°

For melting- and boiling-points of the chlorohydrates, see B. **31**, 1699.

The xylidin used industrially for making azo-dyes, and obtained from dimethyl-aniline, is chiefly m-xylidin and p-xylidin (B. **18**, 2664, 2919). Concerning the separation of isomeric xylidins from each other, see C. 1899, II. 1113.

Amido-polymethyl-benzols $(CH_3)_3C_6H_2NH_2$. The product industrially obtained by heating xylidin chloride, with methyl alcohol, to 250°, under pressure, consists essentially of s-pseudo-cumidin and mesidin, and is used for preparing red azo-dyes (B. **15**, 1011, 2895).

s-Pseudo-cumidin [$5NH_2$, 1, 2, 4], m.p. 68°; b.p. 235°; acetic compound, m.p. 164° (B. **18**, 92, 2661).

Mesidin [$2NH_2$, 1, 3, 5], liquid, b.p. 230°; acetic compound, m.p. 216° (B. **18**, 2229; **24**, 3546).

Duridin [$3NH_2$, 1, 2, 4, 5], m.p. 75°, b.p. 261°–262°; acetic compound, m.p. 207° (B. **42**, 4160).

Isoduridin [$4NH_2$, 1, 2, 3, 5], m.p. 23°, b.p. 255°; acetic compound, m.p. 215° (B. **18**, 1149).

Prehnidin [$5NH_2$, 1, 2, 3, 4], m.p. 64°, b.p. 260°; acetic compound, m.p. 170° (B. **21**, 644, 905).

Amido-pentamethyl-benzol, m.p. 151°, b.p. 277°; acetic compound, m.p. 213° (B. **18**, 825).

Aniline homologues with larger alcohol radicles are obtained not only from the corresponding nitro-compounds by reduction, but also from aniline itself by a nuclear synthesis, when aniline is heated to 250°–280°, with aliphatic alcohols, and zinc chloride. The alkyl takes up the p-position with respect to the amido-group. If iso-butyl and iso-amyl alcohol are used, p-terti-butyl- and p-terti-amyl aniline are produced, water being probably first given off, with formation of iso-butylene, and β-iso-amylene, respectively, which, under the influence of the condensing agent, attach themselves to the p-carbon atom of the aniline.

p-Amido-ethyl-benzol $C_2H_5C_6H_4NH_2$, m.p. −5°, b.p. 216° (B. **22**, 1847).

p-Amido-propyl-benzol, b.p. 225°; acetic compound, m.p. 87° (B. **17**, 1221).

p-Amido-iso-propyl-benzol, b.p. 225°; acetic compound, m.p. 102° (B. **21**, 1159).

p-Amido-tert.-butyl-benzol, m.p. 17°, b.p. 240°; acetic compound, m.p. 172° (B. **24**, 2974).

p-Amido-octyl-benzol, m.p. 19°, b.p. 310°; acetic compound, m.p. 93° (B. **18**, 135).

B. Secondary and Tertiary Phenylamines and Phenyl-Ammonium Bases.

Phenyl-alkylamine.—Modes of formation :—(1) The alkyl products of aniline, and its homologues, are formed, like the aliphatic amines (Vol. I.), by the action of alkyl bromides and alkyl iodides upon primary bases, mostly even at ordinary temperatures. They can also be obtained by heating aniline chlorohydrate, or, better, aniline bromohydrate (B. **19**, 1939), with alcohols, to 250°, alkyl chlorides or bromides being first formed, which then act upon the aniline.

(2) The above method yields the haloid salts of mono- and di-alkyl-aniline together. To obtain mono-alkyl-anilines separately, a start is made from the aceto-compounds of the primary bases. These are dissolved in toluol or xylol, and the calculated quantity of sodium is introduced into the solution. Hydrogen is developed, and white solid Na acetanilide is formed, and transformed smoothly with iodo-alkylene. By saponification of the alkyl acetanilide, the alkyl-aniline is obtained:

$$C_6H_5N\begin{cases}COCH_3\\H\end{cases} \xrightarrow{Na} C_6H_5N\begin{cases}COCH_3\\Na\end{cases} \xrightarrow{ICH_3} C_6H_5N\begin{cases}COCH_3\\CH_3\end{cases} \longrightarrow C_6H_5N\begin{cases}H\\CH_3\end{cases}.$$

Separation of the Primary, Secondary, and Tertiary Bases.—From the acid solution of a mixture, the secondary bases are precipitated, by sodium nitrite, as oily nitrosamines, while the primary ones become diazonium chlorides soluble in water, and the tertiary amines become chlorohydrates (also soluble) of p-nitroso-dialkyl-anilines. From the precipitated nitrosamines the secondary bases can be recovered, by means of tin and HCl. Hydro-ferro-cyanic salts (A. **190**, 184), and

meta-phosphates, may also be used for this separation (B. **10,** 795; **22,** 605; **26,** 1020).

Phenyl-alkyl-ammonium Bases.—The tertiary phenyl-alkylamines, like $C_6H_5N(C_2H_5)_2$, may be combined with alkyl haloids to Am compounds, from which Am hydroxides are generated by action of moist silver oxide or lime:

$$C_6H_5N(C_2H_5)_3I \text{ gives } C_6H_5N(C_2H_5)_3OH.$$

In homologous anilines, containing the substituents in ortho-position with respect to the amine group, the formation of quaternary Am bases is partly difficult, and partly impracticable (B. **33,** 345; cp. **34,** 1129); this accords with a number of other impediments to reaction set by ortho-substituents. A number of phenyl-alkyl-ammonium bases with three different alkyl radicles, *e.g.* phenyl-methyl-alkyl-ethyl-ammonium hydroxide, may be decomposed by fractional crystallisation, of their bromo-camphoro-sulphonic salts, into optically active nitrogen compounds. Their solutions, especially in solvents containing hydroxyl, show a strong tendency to auto-racemisation, thus tending to a gradual loss of optical activity.

Di-alkyl-aniline Oxides.—Prepared from the di-alkyl-anilines, by oxidation with hydrogen peroxide, or sulpho-mono-per-acid (B. **35,** 1082). They correspond to trimethyl-amino-oxide $(CH_3)_3NO$ (Vol. I.), and the alkyl-piperidin oxides (*q.v.*). Methyl groups, in the o-position, retard the formation of dialkyl-aniline oxides (B. **39,** 4285). With acids they form additive salts, *e.g.* **Dimethyl-phenyl-oxy-ammonium-chlorohydrate** $C_6H_5N(CH_3)_2\langle^{OH}_{Cl}$. They easily part with their oxygen, and, therefore, act as oxidisers. On heating dimethyl-aniline oxide, or its chlorohydrate, it breaks up into dimethyl-aniline and oxygen. But the latter acts as an oxidiser on the former, so that a number of other decomposition products are formed. On heating dimethyl-aniline oxide with concentrated sulphuric acid, o- and p-dimethyl-amido-phenol are generally formed (B. **34,** 12). With nitrous and sulphurous acids, addition products are first formed, which, however, are immediately transposed into nuclear substitution substances: nitro-dimethyl-aniline and dimethyl-aniline-sulpho-acid (B. **32,** 342, 1882).

Methyl-ethyl-aniline oxide $C_6H_5(CH_3)(C_2H_5)NO$ has been split up, by means of bromo-camphoro-sulpho-acid, into a dextro-rotatory and a lævo-rotatory base. This is the first case of a compound of 5-valent nitrogen occurring in optically active forms, in which not all the five valencies are saturated by different radicles.

Properties and Transformations.—The most important compounds of this class are the methyl- and ethyl-anilines. Freshly distilled, they are colourless, highly refractive liquids, which gradually turn brown in the light. They smell somewhat like aniline, but less pleasant.

The **secondary phenyl-alkylamines** recall in their behaviour the dialkylamines (Vol. I.). (1) They form salts, and combine with the halogen alkyls to form haloid salts of the tertiary amines. (2) By acid chlorides, and acid anhydrides, the imide hydrogen is made to give way to acid radicles. (3) With nitrous acid they yield nitrosamines (Vol. I.).

The **tertiary phenyl-dialkylamines** containing an aromatic H atom in para-position to the dialkyl-amido-group, show a remarkable mobility of this H atom, which enables it to produce a variety of reactions impossible, or difficult, in the case of the primary and secondary anilines. The greatest theoretical and technical importance is attached to the behaviour of phenyl-dialkylamines towards nitrous acid. The latter converts the phenyl-dialkylamines into p-nitroso-compounds.

The primary, secondary, and tertiary aromatic amines differ in their behaviour towards nitrous acid in the following particulars :

(1) Primary phenylamines gives *diazo*-compounds, and *diazo-amido*-compounds.

(2) Secondary phenyl-alkylamines give *nitrosamines*.

(3) Tertiary phenyl-dialkylamines give *p-nitroso*-compounds.

Some other reactions of phenyl-dialkylamine are mentioned in connection with dimethyl-aniline.

The methyl- and ethyl-anilines have the following boiling-points and densities :

Monomethyl-aniline,	liquid,	b.p. 192°,	D. 0·976 (15°)
Dimethyl-aniline,	m.p. 0·5°,	,, 192°,	,, 0·9575 (20°–24°)
Ethyl-aniline,	liquid,	,, 206°,	,, 0·954 (18°)
Diethyl-aniline,	,,	,, 213·5°,	,, 0·939 (18°).

The methylated anilines are used in industry for the production of aniline dyes, and are obtained by heating aniline chlorohydrate and methyl-alcohol to 220°, or by leading methyl chloride into boiling aniline.

Methyl-aniline $C_6H_5NHCH_3$, by reduction of *phenyl-carbylamine* and *formaldehyde-aniline*. Chlorohydrate, m.p. 122°, obtained from the etheric solution of the base with dry HCl (B. **30,** 3134 ; C. 1898, II. 479). Not coloured by chloride of lime. On heating to 330° it passes into p-toluidin. For methyl-phenyl-nitrosamine and methyl-acetanilide, see below.

By oxidation with hydrogen peroxide or monopersulphonic acid the alkyl groups are split off, from methyl- and ethyl-aniline, and we obtain β-phenyl-hydroxylamine, nitroso- and nitro-benzol, azoxy- and azo-benzol (B. **35,** 703).

With formaldehyde and HCl, methyl- and ethyl-aniline form $C_6H_5N(CH_3)CH_2Cl$ and $C_6H_5N(C_2H_5)CH_2Cl$, which, by reduction, can be converted into dimethyl- and methyl-ethyl-aniline (C. 1902, II. 340 ; 1905, I. 227).

Dimethyl-aniline $C_6H_5N(CH_3)_2$ is also formed on heating bromo- or iodo-benzol with dimethylamine to 250°–260° (C. 1898, II. 478). With dry HCl it yields a mono- and a dichlorohydrate, $C_6H_5N(CH_3)_2.HCl$ and $C_6H_5N(CH_3)_2.2HCl$, crystalline bodies deliquescing in moist air, which easily give off HCl (B. **30,** 3134). Iodo-hydrate, m.p. 112°, cp. C. 1898, II. 479. Not coloured by hypochlorite. With methyl iodide it combines to form trimethyl-phenylium iodide $C_6H_5N(CH_3)_3I$. Treated with nitrous acid it passes into *p-nitroso-dimethyl-aniline*, and, with nitric acid, into *p-nitro-dimethyl-aniline*. With acetyl and benzoyl bromides it gives acetyl- and benzoyl-monomethyl-aniline, besides trimethyl-phenyl-ammonium bromide (B. **19,** 1947). By hydrogen peroxide and monopersulphonic acid it is oxidised to :

Dimethyl-aniline oxide $C_6H_5N(CH_3)_2O$, m.p. 153°. *Picrate*, m.p. 135°; *chlorohydrate*, m.p. 125°.

Dimethyl-aniline has been introduced into a number of condensation reactions. With chloral it combines to *p-amido-mandelic acid* $(CH_3)_2N[4]C_6H_4[1]CH(OH).CCl_3$. With phosgene it passes into *tetramethyl-p-diamido-benzo-phenone* $[(CH_3)_2N[4]C_6H_4[1]]_2CO$; with formic ester and zinc chloride, into *hexamethyl-p-leukaniline* $CH[C_6H_4N(CH_3)_2]_3$; and with benzo-trichloride, into *malachite green* (*q.v.*).

The homologous mono- and dialkyl-anilines behave similarly. We may mention **Methyl-ethyl-aniline** $C_6H_5N(CH_3)(C_2H_5)$, b.p. 201°. Its compound with CH_3I is identical with dimethyl-aniline-ethyl iodide; from which, and others, theoretical conclusions can be drawn with regard to the equivalence of the five nitrogen affinities (cp. B. **33**, 1003). By heating with KHO, the higher alkyl is split off from these Am iodides.

Methyl-ethyl-aniline oxide $C_6H_5(CH_3)(C_2H_5)NO$, from methyl-ethyl-aniline and hydrogen peroxide; colourless and very hygroscopic prisms. *Chlorohydrate*, m.p. 124°; *picrate*, m.p. 148°. On the splitting of the base into optically active components, see above.

Alkylene-mono- and dianilines are obtained from dibromo-paraffins with anilines; [1, 4]-dibromides react with formation of cyclic alkylene imides, or pyrrolidins (Vol. I.), unless a substituent is in the *ortho*-position to the amido group ("steric hindrance," see B. **32**, 848, 2251).

Ethylene-monophenyl-diamine $NH_2.CH_2.CH_2.NHC_6H_5$, b.p. 263°, from phthalimide of potassium (B. **24**, 2191). **Ethylene-diphenyl-diamine** $C_6H_5NH.CH_2.CH_2.NHC_6H_5$, m.p. 65°. **Trimethylene-diphenyl-diamine** $C_6H_5NH[CH_2]_3NHC_6H_5$, b.p.$_{16}$ 280°–285°, besides **Trimethylene-phenylimine**, from trimethylene bromide and aniline. **1, 4-Pentylene-di-o-toluidin** $CH_3C_6H_4NH.CH_2.CH_2CH_2CH(CH_3)NHC_6H_4CH_3$, b.p.$_{23}$ 191°–193°.

Further cyclic alkylene-dianilines like $[CH_2]_2\langle{}^{N(C_6H_5)}_{N(C_6H_5)}\rangle CH_2$, m.p. 124°, and $[CH_2]_3\langle{}^{N(C_6H_5)}_{N(C_6H_5)}\rangle CH_2$, m.p. 87°, **Diphenyl-hydro-glyoxalins** and **-pyrimidins**, have been obtained from alkylene-dianilines with aldehydes (B. **31**, 328; **32**, 2256).

Alkylidene-dianilines are easily obtained, in cold aqueous solutions, from fatty aldehydes (1 mol.) and anilines (2 mols.). They are decomposed by mineral acids. The methylene-dianilines, heated with concentrated HCl, or the corresponding aniline chlorohydrates, are transformed into diamido-diphenyl-methanes (B. **41**, 2145):

$$C_6H_5NH.CH_2.NHC_6H_5 \rightarrow [C_6H_5NH.CH_2.C_6H_4NH_2] \rightarrow NH_2C_6H_4.CH_2.C_6H_4NH_2.$$

The simpler alkylene-dianilines easily pass into the alkylidene-monoanilines, or their transformation products.

Methylene-diphenyl-diamine $CH_2(NHC_6H_5)_2$, m.p. 65°, b.p.$_{12}$ 160°, oxidised with monopersulphonic acid, gives several fission products, and also diphenyl-oxy-form-amidin (B. **35**, 714). **Methylene-o_2-** and **p_2-ditolyl-diamine**, m.p. 52° and 89°. **Ethylidene-diphenyl-diamine** $CH_3CH(NHC_6H_5)_2$, m.p. 51°. **Trichlor-ethylidene-diphenyl-diamine** $CCl_3CH(NHC_6H_5)_2$, m.p. 107°.

Alkylidene-monoanilines are formed by an energetic reaction, by

combination of equimolecular amounts of fatty aldehydes and anilines, with elimination of water ; the simple bodies are mostly unstable oils, which at once either polymerise, like formaldehyde-aniline, or condense, like aldol.

With sulphurous acid and sodium disulphite, the alkylidene-anilines act like the aldehydes, but the reaction is more complicated in the higher homologues of the aldehyde derivatives ; from ethylidene-aniline we obtain $CH_3CH\begin{matrix}NHC_6H_5\\SO_3H\end{matrix}$, the Na salt of which is also formed from acetaldehyde sodium bisulphite, with aniline. The simple, as well as the polymeric, alkylidene-anilines easily add hydrocyanic acid, with formation of the nitrites of α-anilido-carboxylic acids, also obtained by direct transformation of aniline salts, with aldehydes, and CNK (B. **37,** 4073 ; **39,** 986, 2796). The aldoloid condensation products, on the other hand, do not add HCN ; they behave like di-acid, di-secondary bases ; they do add bromine, and must therefore be regarded as probably dianiline derivatives of the olefin-glycols, *e.g.* $CH_3CH(NHC_6H_5)CH : CH(NHC_6H_5)$. These bodies are easily condensed with further elimination of aniline to quinolin derivatives (B. **25,** 2020 ; A. **316,** 89 ; **318,** 58 ; C. 1902, I. 911).

Anhydro-formaldehyde-aniline $(CH_2NC_6H_5)_3$, m.p. 140°, obtained by mixing formaldehyde solution with aniline in the cold. May be reduced to methyl-aniline. Gives with HCN anilido-aceto-nitrile. With aromatic amines the anhydro-formaldehyde anilines condense, in the presence of chlorohydrates, to amido-benzyl-anilines (C. 1900, I. 496) :

$$C_6H_5N : CH_2 + C_6H_5NH_2 \longrightarrow C_6H_5NH.CH_2C_6H_4NH_2.$$

Ethylidene-aniline $CH_3CH : NC_6H_5$, an oil, easily adds hydrocyanic acid to α-anilido-propio-nitrile, and easily condenses to two stereo-isomeric modifications of **β-anilido-butylidene-aniline** $CH_3CH(NHC_6H_5).CH : CHNHC_6H_5$, m.p. 126° and 85°, the latter being easily transformed into the former. On heating with HCl or acetic acid both give quinaldin. With HNO_2 they yield two *dinitroso*-compounds of m.p. 161° and 120°. **Aldonaniline** $CH_3CH(OH)CH_2CH : NC_6H_5$, from aldol and aniline, is a reddish, easily decomposed oil ; by treatment with Am_2S it is transformed into **thio-aldo-aniline** $CH_3.CH(OH)CH_2CH\begin{matrix}NC_6H_5\\S\end{matrix}$, m.p. 92° (B. **29,** 59). For higher homologues, alkylidene-anilines, and aldol-anilines, see B. **33,** 3460 ; **34,** 509 ; C. 1901, II. 582, etc.

C. Poly-Phenylamines.

The modes of formation, and the behaviour, of these compounds are to be illustrated by di- and triphenylamine.

Diphenylamine $NH(C_6H_5)_2$, m.p. 54°, b.p. 310°. (1) This compound, of importance in the aniline-dye industry, was first obtained by A. W. Hofmann, by heating *aniline blue, rosaniline,* and similar dyes (A. **132,** 160). (2) By heating aniline with aniline chlorohydrate to 140°, a large-scale industrial process :

$$C_6H_5NH_2HCl + C_6H_5NH_2 = NH(C_6H_5)_2 + NH_4Cl.$$

In a similar manner *ditolyl-amines* have been prepared (C. 1903, I. 85). (3) By heating aniline with bromo-benzol and copper powder, or

cuprous iodide, good quantities of diphenylamine are obtained. It is well to start from acetanilide, and obtain, first, the acetyl compound, from which the free base is easily separated. (4) By heating aryl-anthranilic acids, with liberation of CO_2 (A. **355,** 312). The last two methods are very suitable for preparing asymmetrical and substituted diphenylamines (B. **40,** 4541).

Diphenylamine is a crystalline body, of pleasant odour. In water it is nearly insoluble, but easily soluble in alcohol and ether.

It is but a weak base, the salts of which are dissolved by water. The imide hydrogen may also be replaced by metals: potassium-diphenyl-amine $(C_6H_5)_2NK$ (C. 1898, II. 1252).

Oxidation of diphenylamine with potassium permanganate, or lead peroxide, in acetone, or benzol solution, gives *tetraphenyl-hydrazin* (B. **39,** 1500). In alkaline solution it is oxidised by potassium permanganate to *diphenyl-p-azophenylene*, or *quinone-dianile* $C_6H_5N=[1]C_6H_4[4]=NC_6H_5$ (B. **20,** R. 719). Chlorine and bromine change diphenylamine into tetra- or hexahalogen substitution products; HNO_3 into the hexanitro-products. H_2SO_4 dissolves diphenylamine, and the solution colours blue with traces of HNO_3 (test for the latter). Heating with sulphur gives *thio-diphenylamine*, $NH\langle^{C_6H_4}_{C_6H_4}\rangle S$ (*q.v.*), the fundamental body of the *thionin* dyes; heating with aliphatic acids to 300° gives acridines (*q.v.*) like $N\langle^{C_6H_4}_{C_6H_4}\rangle CH$.

Diphenylamine is used for preparing *triphenyl-rosaniline* (*q.v.*), or *aniline blue.*

Methyl-diphenylamine $CH_3N(C_6H_5)_2$, b.p. 292° (A. **235,** 21).

Phenyl-p-toluidin $C_6H_5NHC_6H_4CH_3$, m.p. 87°; **Phenyl-m-xylidin** $C_6H_5NHC_6H_3(CH_3)_2$, m.p. 43°, by methods 3 and 4.

Triphenylamine $(C_6H_5)_3N$, m.p. 127°, distils without decomposition, formed by heating dipotassium-aniline, or from sodium-diphenylamine with bromo-benzol (B. **18,** 2156). The easiest method is by heating diphenylamine with iodo-benzol and some powdered copper; or from diphenyl-anthranilic acid by splitting off CO_2 (B. **40,** 2448). It crystallises from ether in large plates. It dissolves in hot H_2SO_4 with intense blue coloration. It does not form salts with acids. Nitrogenation gives a trinitro-product, from which, by reduction, *triamido-triphenylamine* is formed (B. **19,** 759). Phosgene gives *hexaphenyl-rosaniline* (*q.v.*).

p-Tritolyl-amine $(CH_3C_6H_4)_3N$, m.p. 117°, from p-ditolyl-amine and p-iodo-toluol. With Br, PCl_5, $SbCl_5$, etc., it gives dark-blue, unstable addition products, decomposed by water with restoration of tritolyl-amine (B. **46,** 4268).

D. Aniline Derivatives of Inorganic Acids.

Aromatic thionylamines (Michaelis).—These compounds, corresponding to the alkyl-thionylamines (Vol. I.), are obtained by the action of thionyl chloride upon primary bases, a reaction characteristic of these compounds.

The thionyl-anilines are mostly yellow liquids, not decomposing when boiling, even under increased pressure. They have an aromatic odour, pervaded by the sulphur chloride smell.

Thionyl-aniline $C_6H_5N:SO$, b.p. 200°, D_{15} 1·236. **Thionyl-o-chloraniline,** b.p.$_{46}$ 207°; m-compound, b.p. 233°; p-compound, m.p. 36°, b.p. 237°. **Thionyl-o-bromaniline,** b.p.$_{46}$ 210°; m-compound, m.p. 32°; p-compound, m.p. 60°. **Thionyl-o-nitraniline,** m.p. 32°.

Thionyl-o-toluidin, b.p.$_{100}$ 184°; m-compound, b.p. 220°; p-compound, m.p. 7°, b.p. 224° (A. **274,** 201), etc.

Phenyl-sulphaminic acid $C_6H_5NHSO_3H$, known only in its salts, formed (1) by the action of SO_3 or $ClSO_3H$ upon aniline, in chloroform solution (B. **24,** 360); (2) by heating aniline with amido-sulphonic acid (B. **27,** 1244); (3) by combining β-phenyl-hydroxylamine with SO_2; (4) by action of sodium bisulphite, or hydro-sulphite, upon aqueous solutions of benzol (C. 1904, I. 1380; 1906, II. 37).

$$C_6H_5NO_2+3HSO_3Na=C_6H_5NHSO_3Na+2SO_4HNa.$$

By dilute acids phenyl-sulphaminic acid is easily split up, with formation of aniline salts; while concentrated acids produce transposition into the o- and p-aniline-sulpho-acid (B. **30,** 2274).

p-Tolyl-sulphaminic acid is precipitated from solution of its Am salts by acids (B. **28,** 3161). p-Chloro-phenyl-sulphaminic acid $ClC_6H_4NHSO_3H$ is, on heating, transposed into **p-Chloraniline-o-sulphonic acid** (B. **34,** 2748). For formation of phenyl-sulphaminic acids from anilines with SO_2, see C. 1898, II. 195. **Sulphanilide** $SO_2(NHC_6H_5)_2$ (B. **28,** 362).

The aromatic **nitroso-amines** and **nitro-amines** are dealt with later, before the diazo-compounds.

Phosphoro-phenylamines. *Phosph-azo-benzol chloride* $C_6H_5N:PCl$, m.p. 136°–137°, by action of PCl_3 upon aniline chlorohydrate. With phenol it yields **Phenoxyl-phosphazo-benzol** $C_6H_5N:P(OC_6H_5)$. With aniline, **Phosphazo-benzol-anilide** $C_6H_5N:P.NHC_6H_5$ (B. **27,** 490). **Anilido-phosphoric dichloride** $C_6H_5NH.POCl_2$, m.p. 84°, from $POCl_3$ and aniline chlorohydrate (B. **26,** 2939). **Ortho-phosphoric anilide** $(C_6H_5NH)_3PO$, m.p. 208° (A. **229,** 334). **Oxy-phosphazo-benzol-anilide** $C_6H_5NH.PO:NC_6H_5$, m.p. 357°, is the final product of the action of $POCl_3$ upon aniline (B. **29,** 716; A. **326,** 129). From aniline chlorohydrate and PCl_5 we get **trichloro-phosphanile** $C_6H_5N.PCl_3$ (B. **28,** 2212; cp. C. 1902, II. 355).

Sulpho-phosphazo-benzol chloride $C_6H_5N:PSCl$, m.p. 149°, b.p. 280°–290°, from $PSCl_3$, and aniline chlorohydrate (B. **29,** 1239).

Arseno-phenylamines are produced by the action of arsenious chloride or bromide upon aniline in ether or chloroform.

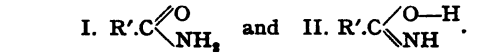
Arsen-anilido-dichloride $C_6H_5NHAsCl_2$, m.p. 87°. **Arsen-anilido-dibromide,** m.p. 112°. **Arsen-dianilido-monochloride** $(C_6H_5NH)_2AsCl$, m.p. 127°. **Arsen-anilido-dimethyl-ether** $C_6H_5NHAs(OCH_3)_2$, b.p.$_{12}$ 55° (A. **261,** 279).

Silico-tetraphenylamide $Si(NHC_6H_5)_4$, m.p. 137° (B. **22,** R. 746), passes on heating into **Silico-diphenylimide** $Si(NC_6H_5)_2$ (C. 1903, I. 572).

E. Carboxylic Derivatives of the Aromatic Primary and Secondary Amines.

In the introduction to the fatty acids, it was explained, by the example of acetic acid, which nitrogen derivatives could be obtained

by changes in the carboxyl group. The first category of compounds are the carboxylic amides, which may be variously interpreted, according to the formulæ :

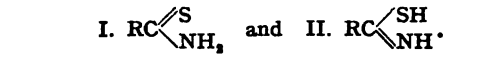


The imido-ethers are derived from formula II.

Many such fatty-acid derivatives have been obtained, by starting from aniline and its primary homologues. For the acid amides of secondary bases only formula I. need be considered. In a primary amine the two H atoms may be replaced by acid radicles.

The introduction of the second acidyl group is facilitated by o-substituents in the aniline nucleus, which otherwise retard the entry of the first acidyl group (C. 1901, I. 836).

To the acid amides correspond the thiamides and iso-thiamides :

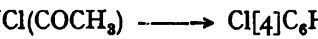


These classes of bodies are followed by the amido-chlorides, the imido-chlorides, and the amidins.

Anilides of mono-basic fatty acids.—The anilides or phenylamides of the fatty acids are produced by the same methods (Vol. I.) as the acid amides themselves : (1) by heating the aniline salts of the fatty acids ; (2) by the action of aniline upon esters ; (3) upon acid chlorides ; (4) upon acid anhydrides ; (5) by action of acid esters upon C_6H_5NHMgI (C. 1904, II. 201).

The acid amides are very stable ; they mostly distil without decomposition, and can be chlorinated, brominated, and nitrogenated direct. They serve for the simple and quick identification of the aromatic bases. By heating with alkalies, or with HCl, the anilides are again split into their components. Boiling with sulphur converts them into benzol-thiazols (*q.v.*).

The secondary anilides, like the secondary alkyl-anilines, form nitroso-anilides with nitrous acid. With phenol, and sulphuric acid, they give the nitrosamine reactions, but they are much less stable than the nitrosamines of the secondary anilines ; by reducing agents the nitroso-group is split off again. With hypochlorous and hypobromic acids, the hydrogen attached to the nitrogen of the anilides may be replaced by halogens : $C_6H_5.NCl.COCH_3$; these nitrogen haloids are easily transposed under the influence of HCl, or sunlight, into anilines with nuclear substitution, *e.g.*



(B. **32**, 3573 ; C. 1903, I. 21, 141).

Formanilide $C_6H_5NH.CHO$, m.p. 46°, b.p. 284° (A. **270**, 279), is produced on boiling aniline with formic acid, or during rapid heating of aniline with oxalic acid. It is soluble in water, alcohol, and ether.

Salts and alkyl derivatives.—From the aqueous solution, NaHO precipitates **Sodium formanilide** $C_6H_5N : (CHONa)$, in a crystalline form, and with methyl iodide this gives **Methyl formanilide** $C_6H_5N\langle^{CHO}_{CH_3}$, m.p. 12·5°, b.p. 253°. By heating with alcoholic potash, or HCl, the latter is split into acid, and methyl-aniline (B. **21**, 1107).

Silver formanilide $C_6H_5N:CH(OAg)$ is precipitated from the alcoholic solution of the sodium compound with silver nitrate, and passes, in the presence of methyl iodide, into **Methyl iso-formanilide** $C_6H_5.N:CHOCH_3$, b.p. 196°, which, on heating, is transposed into the isomeric methyl formanilide (B. **23,** 2274, R. 659). But the silver salt gives N derivatives with acid chlorides, like benzoyl chloride (B. **29,** R. 1141). **Ethyl iso-formanilide,** *ethoxy-methylene-aniline,* $C_6H_5N:CHOC_2H_5$, b.p. 212°, is also obtained by prolonged boiling of aniline with ortho-formic ester, besides diphenyl formamidin (A. **287,** 360).

Acetanilide, *antifebrin* $C_6H_5NHCOCH_3$, m.p. 114°, b.p. 295°, generated by boiling aniline with glacial acetic acid (B. **15,** 1877); or from aniline with acetyl chloride, acetic anhydride, or thio-acetic acid; the last of these agents has been found very useful for introducing acetyl groups into aniline (B. **35,** 110).

Acetanilide is also formed from malon-anilic acid by rejection of CO_2. A notable method is by treating the isomeric aceto-phenone oxime with sulphuric acid at 100° (B. **26,** 2581):

$$C_6H_5C:(NOH).CH_3 \longrightarrow C_6H_5NH.CO.CH_3.$$

Crystallised from water, in which it is not easily soluble in the cold, acetanilide does not form white flakes. It is used as an anti-pyretic and anti-rheumatic. For action of PCl_5 see A. **184,** 86. Heating with sulphur produces bis-thiazol (*q.v.*).

Brom-acetanilide, m.p. 131°, yields indigo (*q.v.*) on melting with caustic potash in air.

Salts.—The **chlorohydrate** is decomposed by water. On heating, it passes into diphenyl-acet-amidin, flavanilin (*q.v.*) and dimethyl-quinolin (B. **18,** 1340). With sodium ethylate, on heating, it is converted into ethyl-aniline and sodium acetate (B. **19,** R. 680).

Sodium acetanilide $C_6H_5N:C(ONa)CH_3$, by action of sodium upon the xylol solution of acetanilide, yields mono-alkyl-acetanilides with alkylene iodide, and from these the mono-alkyl-anilines may be obtained (B. **10,** 328; **23,** 2587). The same acetanilides are produced by the action of acetic anhydride upon the secondary bases. But acetanilide, heated with silver oxide, methyl iodide, or dimethyl sulphate, yields **Aceto-phenyl-imido-methyl-ether** $CH_3C\begin{matrix}NC_6H_5\\OCH_3\end{matrix}$, b.p. 197° (C. 1901, I. 1043; A. **333,** 293). **Mercurio-acetanilide** $(C_6H_5NCOCH_3)_2Hg$ (B. **28,** R. 113).

Methyl-acetanilide, *exalgin,* m.p. 101°, b.p. 253° (anti-neuralgic). **Ethyl-acetanilide,** m.p. 54°, b.p. 258°. **n-Propyl-acetanilide,** m.p. 47°, b.p. 266° (B. **21,** 1108).

Substituted Acetanilides.—The action of Cl, Br, and HNO_3 upon acetanilide produces o- and p-derivatives.

Formyl acetanilide $C_6H_5N(COH)(COCH_3)$, m.p. 56°, from mercurio-formanilide and acetyl chloride (B. **29,** R. 1155).

Diacetanilide $C_6H_5N(COCH_3)_2$, m.p. 37°, $b.p._{11}$ 142°, by heating acetanilide with acetyl chloride to 170°–180°, or with acetic anhydride; also by boiling phenyl-mustard oil with acetic anhydride (B. **27,** 91; **28,** 1665). Its physiological effects are similar to those of acetanilide (B. **31,** 2788).

Concerning transpositions of diacetanilide into **p-Acetamido-**

acetophenone, $(CH_3CO)_2NC_6H_5 \longrightarrow CH_3CONHC_6H_4COCH_3$, see C. 1902, II. 355; 1903, I. 1222.

The acetic compounds are distinguished for their power of crystallisation. They serve as means of recognising many primary and secondary aromatic bases. Hence the melting-points of many acetic compounds have been quoted in connection with the bases concerned.

Thio-anilides are formed from the anilides with P_2S_5; or from amidins and isonitrites with H_2S; or from phenyl-mustard oil with magnesium-alkyl iodides.

Thio-formanilide C_6H_5NHCHS melts at 137°, with decomposition into H_2S and phenyl iso-cyanide (B. **11,** 338; A. **192,** 85). For homologous thio-formanilides, see B. **18,** 2292.

Thio-acetanilide, m.p. 75°, oxidised with potassium ferricyanide, passes into **Amido-thio-phenol** $C_6H_4\langle^{N}_{S}\rangle C.CH_3$ (B. **19,** 1072). Thio-anilides of homologous fatty acids, B. **36,** 587. **Methyl-thio-acetanilide,** m.p. 59°, b.p. 290°.

Methyl-iso-thio-acetanilide $C_6H_5N:C\langle^{CH_3}_{SCH_3}$, b.p. 245°, **Ethyl-iso-thio-acetanilide,** b.p. 250°, formed by action of sodium alcoholate and alkyl iodides upon thio-acetanilide. On shaking with HCl they decompose into aniline chlorohydrate and *thio-acetic ester* (Vol. I.) (B. **12,** 1061).

F. Phenylated Amidins of Formic Acid and Acetic Acid.

Besides the general methods of amidin formation, enumerated in Vol. I., the phenylated amidins are prepared by action of PCl_3 or HCl upon a mixture of aniline and anilide, with liberation of water (B. **15,** 208, 2449):

$$C_6H_5NHCOCH_3 + C_6H_5NH_2 = \begin{matrix} C_6H_5NH \\ C_6H_5N \end{matrix}\rangle C.CH_3 + H_2O.$$

They are feeble bases, and combine with 1 equiv. HCl to form salts. On boiling with alcohol they decompose into aniline and acid anilides.

Diphenyl-formamidin, *methenyl-diphenyl-diamine* $C_6H_5N:CH.NHC_6H_5$, m.p. 135°, by heating aniline to 180° with chloroform or formic acid; from hydrocyanic sesqui-chlorohydrate $(CHN)_2(HCl)_3$ with aniline (B. **35,** 2498); or by boiling phenyl-iso-cyanide $C_6H_5.NC$ with aniline. It crystallises from alcohol in long needles, and distils at about 250°, with partial decomposition, into benzo-nitrile and aniline.

Di-aryl-formamidins are distinguished from the amidins of the higher carboxylic acids by their superior power of reaction. With the CH_2 group of malonic ester, aceto-acetic ester, and similar substances, they react with liberation of aniline, and formation of aniline-methylene derivatives like: $C_6H_5NHCH:C(CO_2R)_2$ **Anilino-methylene-malonic ester,** $C_6H_5NHCH:C(COCH_3)CO_2R$ **Anilino-methylene-acetic ester,** etc. (B. **35,** 2505).

Diphenyl-oxy-formamidin melts without water at 131°; formed

from methyl-iso-formanilide with β-phenyl-hydroxylamine ; also from methylene-diphenyl-hydroxylamine by withdrawing H_2O, by means of anhydrous copper sulphate. Acetic anhydride transposes it into diphenyl-urea $C_6H_5NH.CO.NHC_6H_5$ (B. **35,** 1451, 1874).

Diphenyl-ethenyl-amidin melts at 131°, formed by addition of $CH_3.MgI$ to carbo-diphenyl-imide (*q.v.*).

Phenyl-ethenyl-amidin $C_6H_5.N : C(NH_2).CH_3$, from aceto-nitrile and HCl-aniline (A. **184,** 362 ; **192,** 25) (Vol. I.) is liquid.

Phenylisuretin $C_6H_5NH.CH : NOH$, m.p. 138°, from formyl-chloridoxime (Vol. I.) with aniline (B. **27,** R. 745).

PHENYLATED CARBYLAMINES (Vol. I.).—**Phenyl-isocyanide,** *phenyl-carbylamine,* boils, at atmospheric pressure, at 166° with strong polymerisation, below 20 mm. at 64° without change. The colourless liquid, D_{15} 0·977, soon colours a light blue, then dark blue, and turns resinous. Phenyl-isocyanide is formed from aniline and chloroform, with alcoholic potash, also by heating thio-formanilide. Phenyl-carbylamine has an abominable and clinging odour, tastes bitter, and causes headache and flow of saliva. It behaves as follows :—Heating to 220° transposes it into *benzo-nitrile* C_6H_5CN. Nascent H converts it into *methyl-aniline.* With HCl in dry ether it gives *phenyl-imido-formyl-chloride* ; with glacial acetic acid, *formanilide* ; with SH_2 at 100°, *thio-formanilide* ; with sulphur at 130°, *mustard oil* ; with aniline at 170°, *diphenyl-formamidin* ; with chlorine, *isocyano-phenyl-chloride* or *phenyl-amido-carbonyl-chloride* ; with phosgene, *meso-xanil-amido-chloride* ; with acetyl chloride, *pyro-racemic anilide chloride* (Nef, A. **270,** 274). **o-Tolyl-isocyanide,** b.p.$_{16}$ 75°, D_{24} 0·968. **p-Tolyl-isocyanide,** b.p.$_{32}$ 99° (B. **27,** R. 792).

PHENYLAMINE DERIVATIVES OF OXY-ACIDS.—These compounds are capable of some condensation reactions, in which the benzene H atom, in *ortho*-position to nitrogen, often takes part, so that heterocyclic compounds are formed. The acids are obtained by heating the corresponding halogen fatty acids with anilines (cp. B. **30,** 2303, 2464, 3169 ; **31,** 2678). Their nitriles are formed : (1) by addition of HCN to the alkylidene-anilines ; (2) from the bisulphite addition-products of the latter with CNK (C. 1902, II. 315 ; B. **37,** 4073) ; (3) by heating the aldehyde and ketone cyano-hydrins with aniline ; (4) by direct transformations of aniline salts with aldehydes, or ketones, and CNK (B. **39,** 986, 2796).

Anilido-acetic acid, *phenyl-glycocoll, phenyl-glycin* $C_6H_5NHCH_2COOH$, m.p. 127°, by heating chloro- or bromo-acetic acid with aniline and water (B. **10,** 2046 ; **21,** R. 136). Its alkyl esters are obtained by heating aniline with chloracetic ester or dichloro-vinyl ether in aqueous suspension (C. 1908, I. 1006 ; II. 358), or by action of diazo-acetic ester upon aniline. Its **nitrile,** m.p. 43°, is formed (1) from anhydro-formaldehyde-aniline with absolute HCN ; (2) from its bisulphite compounds with CNK ; (3) from formaldehyde-cyanhydrin with aniline ; (4) from aniline chlorohydrate, formaldehyde, and CNK (C. 1902, II. 315 ; 1903, I. 208 ; 1904, I. 1308). By heating the free acid to 150° we obtain **Diphenyl-glycin-anhydride** or **diphenyl-diacipiperazine** $C_6H_5N\langle\begin{matrix}CH_2—CO\\CO—CH_2\end{matrix}\rangle NC_6H_5$, m.p. 263° (B. **25,** 2270). Phenyl-glycin possesses industrial importance, since, on melting with caustic potash,

or, better, sodium amide, it passes into *indoxyl* $C_6H_4\langle^{C(OH)}_{NH}\rangle CH$, which, in air, easily oxidises to *indigo*.

Distillation of calcium anilido-acetate with Ca formate gives indol $C_6H_4\langle^{CH}_{NH}\rangle CH$.

Besides phenyl-glycin we obtain from aniline and chloracetic acid **Diglycol-phenyl-amidic acid,** *anilino-diacetic acid* $C_6H_5N(CH_2COOH)_2$, m.p. 150°–155°. Oxidised with MnO_4K it gives **Formyl-phenyl-glycin** $C_6H_5N(CHO)CH_2COOH$, m.p. 125°. It is better obtained from phenyl-glycin by heating with formic acid (B. **34,** 1647).

Diglycol-phenyl-amidic anhydride $C_6H_5N(CH_2CO)_2O$, m.p. 148° (B. **25,** 2272); **imide,** $C_6H_5N(CH_2CO)_2NH$, m.p. 158° (B. **22,** 1809); **anile** $C_6H_5N(CH_2CO)_2NC_6H_5$, m.p. 152° (B. **22,** 1802). Isomeric with diglycol-phenyl-amidic acid is **Diglycol-anilic acid** $O\langle^{CH_2CONHC_6H_5}_{CH_2CO_2H}$, m.p. 118°, from diglycolic anhydride and aniline. With acetyl chloride it passes into **Diglycolic anile** $O(CH_2CO)_2NC_6H_5$, m.p. 116°, isomeric with diglycol-phenyl-amidic anhydride (A. **278,** 66). **Thio-diglycol-anilic acid** and **anilide,** see A. **278,** 70.

Methyl-phenyl-glycin $C_6H_5(CH_3)NCH_2COOH$, by heating methyl-aniline with chloracetic acid. The nitrile, b.p. 266°, is obtained by the action of methyl-aniline upon formaldehyde-cyano-hydrin. **Amide,** m.p. 163° (B. **37,** 2636).

Dimethyl-phenyl-betain $C_6H_5\overline{N(CH_3)_2CH_2COO}+H_2O$, m.p. 124°, by the action of chloracetic acid upon dimethyl-aniline. On heating it is transformed into **Methyl-phenyl-glycocoll-methyl ester,** $b.p._{10}$ 141°.

o-Nitro-phenyl-glycin $NO_2[2]C_6H_4[1]NHCH_2CO_2H$, m.p. 193°.

α-Anilido-propionic acid, *phenyl-alanin* $C_6H_5NHCH(CH_3)COOH$, m.p. 162°, is obtained from its nitrile, the transformation product of ethylidene-cyano-hydrin with aniline, and of ethylidene-aniline with HCN (B. **15,** 2036; **28,** 2010; **25,** 2032). **α-Anilido-butyric acid** $C_6H_5NHC(CH_3)_2COOH$, m.p. 185°; **nitrile,** m.p. 94° (B. **39,** 989). **β-Anilido-propionic ester,** $b.p._{18}$ 175°, from **β-iodo-propionic ester** (B. **29,** 514). β-Anilido-aliphatic acids are also formed by attachment of aniline to olefin-carboxylic acids (B. **36,** 1262).

Dianilido-acetic acid $(C_6H_5NH)_2CHCOOH$, m.p. 88°–93°, by action of aniline upon diacetyl-glyoxylic acid. It easily splits off 1 mol. aniline and forms anyl-glyoxylic acid. Heating with aniline and its chlorohydrate, it is transformed into p, p-diamido-diphenyl-acetic acid (*q.v.*) (B. **41,** 3031, 4264).

ANILINE DERIVATIVES OF KETONE-CARBOXYLIC ACIDS.—**Pyro-racemic anilide** $CH_3.CO.CONC_6H_5$, m.p. 104°. **Pyro-racemic anilide chloride** $CH_3.CO.CCl:NC_6H_5$, m.p. 136°, from phenyl-carbylamine (*q.v.*) and acetyl chloride (A. **270,** 299). **Anile-pyro-racemic acid** $C_6H_5N:C\langle^{CH_3}_{COOH}$, m.p. 122° with decomposition, formed from aniline and pyro-racemic acid in ether (A. **268,** 126); passes easily into *anile-uvitoninic acid*, a derivative of quinolin.

Aceto-acetic anilide $CH_3CO.CH_2CONHC_6H_5$, m.p. 85°, formed from aceto-acetic ester and aniline at 130°. May be condensed to **γ-methyl-carbostyrile** (*q.v.*). **Anile-aceto-acetic ester,** *β-phenyl-imido-butyric ester*

$C_6H_5N:C\langle^{CH_2CO_2C_2H_5}_{CH_3}$, or **β-Anilido-crotonic ester** $NHC\langle^{CHCO_2C_2H_5}_{CH_3}$, b.p.$_{16}$ 165°, from aniline and aceto-acetic ester at ordinary temperatures. It adds HCN, like the alkylidene-anilines, which speaks for the anile formula (B. **35,** 2080). By alkalies, and acids, it is split up into its generators. By heating at ordinary pressures it may be condensed to γ-oxy-quinaldin (*q.v.*) and phenyl-lutidone-carboxylic acid (*q.v.*) (B. **20,** 947, 1398; **22,** 83). A similar behaviour is shown by the tolyl-amido-compounds.

ANILINE DERIVATIVES OF CARBONIC ACID.—The numerous compounds of this class are treated in the same order as the amine and alkylamine derivatives of carbonic acid, with which they can be thus most conveniently compared (see Vol. I.).

Carbanilic acid, *phenyl-carbaminic acid,* is unknown in the free state. Its salts are obtained by the action of very dilute alkalies, or alkaline-earth hydroxides, upon phenyl isocyanate. On acidulating, even with carbonic acid, the salts immediately break up into aniline and CO_2. Their esters, the **Phenyl-urethanes,** are obtained: (1) from aniline and chloro-carbonic acid esters (B. **18,** 978); (2) from carbanile and alcohols (B. **8,** 654); (3) from urea chlorides and alcohols (B. **24,** 2108); (4) from benzoyl azide with alcohols (cp. Vol. I., and B. **29,** R. 181).

Methyl ester $C_6H_5NH.CO_2CH_3$, m.p. 47°, with sulphuric acid passes into amido-sulpho-benzoic ester (B. **18,** 980). **Ethyl ester,** m.p. 52°.

Urea chlorides are formed from secondary aromatic bases, and phosgene in benzene solution (B. **23,** 424). **Phenyl-urea chloride** $C_6H_5NH.COCl$, m.p. 59°, and **bromide,** m.p. 67° (B. **28,** R. 777). **Methyl-phenyl-urea chloride** $(CH_3)(C_6H_5)N.COCl$, m.p. 88°, b.p. 280°. **Diphenyl-urea chloride** $(C_6H_5)_2N.COCl$, m.p. 85°. With benzene and Al chloride they pass into the amides of benzoic acid (B. **20,** 2118; **24,** 2108); cp. the syntheses of aromatic carboxylic acids. Sodium, in ether, converts **di-p-tolyl-urea chloride,** m.p. 102°, into a tetra-substituted oxamide (B. **25,** 1819, 1825).

PHENYLATED UREAS.—**Phenyl-urea** $NH_2CONHC_6H_5$, m.p. 144°: (1) from cyanic acid and aniline, by evaporation of a solution of aniline chlorohydrate with potassium isocyanate (B. **9,** 820); (2) from ammonia and *carbanile.*

Sym. alkyl-phenyl-ureas are produced by the action of aniline upon isocyanic ester, or of phenyl isocyanate upon alkylamine. **Sym. alkyl-phenyl-urea** $C_2H_5NHCONHC_6H_5$, m.p. 99°.

Asym. alkyl-phenyl-ureas from alkyl-aniline chlorohydrate and potassium isocyanate, as **ethyl-phenyl urea,** m.p. 62°.

Sym. diphenyl-urea, carbanilide $CO(NHC_6H_5)_2$, m.p. 235°, b.p. 260°, formed (1) from phosgene and aniline (B. **16,** 2301); (2) from phenol isocyanate and aniline (A. **74,** 13); (3) from s-diphenyl-sulpho-urea, with mercuric oxide, or alcoholic potash (A. **70,** 148); (4) from aniline, and urea at 170°; (5) from monophenyl-urea, and aniline at 190° (B. **9,** 820); (6) from diphenyl carbonate, with aniline, at 170° (B. **18,** 516); (7) from oxanilide, by heating with HgO (M. **25,** 375); (8) from phenyl isocyanate and water, carbanilide forms needles of a silky lustre, easily soluble in alcohol and ether, slightly soluble in water.

as-Diphenyl-urea $C_6H_5NH.CO.N(C_6H_5)_2$, m.p. 132°, and **Tetraphenyl-urea** $(C_6H_5)_2N.CO.N(C_6H_5)_2$, m.p. 183°, are also obtained from diphenyl-urea (B. **37**, 963).

CYCLIC ALKYLENE-PHENYL-UREA DERIVATIVES (cp. Vol. I.).—**Ethylene-phenyl-urea,** see B. **24**, 2192. **Trimethylene-phenyl-urea** (B. **23**, 1173).

Ethylene-carbanilide $CO<\begin{matrix}N(C_6H_5)CH_2\\N(C_6H_5)CH_2\end{matrix}$, m.p. 183° (B. **20**, 784). **Trimethylene-carbanilide,** m.p. 153° (B. **20**, 783).

Ureïds of the Phenylated Ureas of Mono-carboxylic Acids.—**Acetyl-phenyl-urea** $CH_3CONH.CO.NHC_6H_5$, m.p. 183°, from phenyl-urea with acetic anhydride or acetyl chloride (B. **8**, 1181), and from phenyl isocyanate and **aceto-chloramide** (C. 1904, I. 241). **Acetyl-carbanilide** $C_6H_5NH.CO.N(COCH_3)C_6H_5$, m.p. 115° (B. **17**, 2882).

Ureïds of Oxy-acids.—**Glycol-phenyl-urea,** *phenyl-hydantoïn*, m.p. 194°, from phenyl-glycin and urea at 160°; also from chloracetyl-urethane with aniline (C. 1899, II. 420; *J. pr. Ch.* 2, **66**, 231; homologues, see C. 1906, I. 461). Diphenyl-hydantoïn, m.p. 139° (B. **25**, 2274).

Phenylated Pseudo-Urea Derivatives are obtained from phenylated cyanamides, with alcohols and HCl, as are the imido-ethers from nitriles.

Methyl-phenyl-iso-urea $C_6H_5NHC(OCH_3):NH$, see C. 1901, II. 919. **Ethyl-phenyl-iso-urea** $C_6H_5NH.C(OC_2H_5):NH$, b.p.$_{19}$ 138°. **Ethyl-phenyl-methyl-iso-urea** $C_6H_5N(CH_3).C(OC_2H_5):NH$, b.p.$_{21}$ 137° (B. **32**, 1494; **33**, 807). **Ethyl-diphenyl-iso-urea,** *anilido-phenyl-carbaminic ethyl ether* $C_6H_5N:C(OC_2H_5)NHC_6H_5$, an oil, b.p.$_{20}$ 200°. **Methyl-ditolyl-iso-urea,** m.p. 48°, b.p.$_{11}$ 199°, generated from the carbodi-phenylimides with alcohol at 180°–190°, or, better, with Na alcoholates, give with HCl addition products. By acids they are easily split up, but with alkalies and amines they are stable (C. 1899, I. 828). **Triphenyl-chloro-carbamidin** $ClC<\begin{matrix}NC_6H_5\\N(C_6H_5)_2\end{matrix}$, m.p. 92°, formed by action of PCl_5 upon triphenyl-urea; gives, with Na ethylate, ethyl-iso-triphenyl-urea $C_6H_5N:C(OC_2H_5)N(C_6H_5)_2$, m.p. 49° (B. **37**, 964).

Phenylated Ureïds of Carbonic Acid.—**Phenyl-allophanic ester** $C_6H_5NH.CO.NHCO_2C_2H_5$, m.p. 120° (*J. pr. Ch.* 2, **32**, 18). **Diphenyl-allophanic acid,** see B. **4**, 246. **Sym. Phenyl-biuret** $C_6H_5.N:(CONH_2)_2$, m.p. 192°, from phenyl-urea and PCl_5. **as-Phenyl-biuret** $C_6H_5NH.CONH.CO.NH_2$, m.p. 167° (A. **352**, 73). **Diphenyl-biuret** $C_6H_5NH.CONH.CO.NHC_6H_5$, m.p. 210° (B. **4**, 265), by heating phenyl-urea with excess of phosgene. **Triphenyl-biuret,** m.p. 147° (B. **4**, 250).

PHENYLATED HYDROXYLAMINE AND HYDRAZIN DERIVATIVES OF UREA.—**Phenyl-hydroxyl-urea** $C_6H_5NH.CO.NHOH$, melts at 140° with decomposition, formed from carbonile and hydroxylamine chlorohydrate (A. **263**, 264).

Phenyl-semicarbazide, *phenyl-carbaminic hydrazide* $C_6H_5NH.CO.NH.NH_2$, m.p. 120°, isomeric with carbaminic hydrazide (*q.v.*), formed (1) from its acetyl derivative, m.p. 169°, formed on boiling benzo-acid with aceto-hydrazide in acetone, with liberation of nitrogen:

$$C_6H_5CON_3+NH_2NH.COCH_3=C_6H_5NH.CO.NHNH.COCH_3+N_2;$$

(2) by splitting up acetone phenyl-semicarbazone $(CH_3)_2C:NNH.CO.NHC_6H_5$, which is easily obtained by heating aniline with acetone semi-carbazone (B. **38**, 831); (3) from phenyl-urea with hydrazin hydrate.

Hydrazi-dicarbon-anilide $C_6H_5NH.CO.NHNH.CONHC_6H_5$, m.p. 245°, from phenyl-semicarbazide by heating; it is oxidised to **azo-di-carbon-anilide** $C_6H_5NHCO.N:N.CONHC_6H_5$, m.p. 183°. **Phenyl-carbamic azide** $C_6H_5NH.CON_3$, m.p. 104°. In contrast with other carboxylic azides it is split by water, or alcohol, into nitrogen hydride, and carbaminic acid, and their esters (*J. pr. Ch.* 2, **58**, 205).

PHENYLATED DERIVATIVES OF THE THIO-CARBAMINIC ACIDS AND OF THIO-UREA.—**Phenyl-carbaminic thio-methyl ester** $C_6H_5.NH.COSCH_3$, m.p. 83°, and ethyl ester, m.p. 74°, from diphenyl-amidin-thio-alkylene, heated with dilute sulphuric acid to 180° (B. **15**, 339).

Phenyl-sulphur-ethane, *xanthogen-anilide, thio-carbanilic ethyl ester* $C_6H_5NHCS.OC_2H_5$ or $C_6H_5N:C(SH)OC_2H_5$, m.p. 71°, from phenyl-mustard oil, with alcohol at 120°, or with alcoholic potash. With primary and secondary bases it changes into phenyl-sulpho-ureas. On distilling, it decomposes into phenyl-mustard oil and alcohol (B. **15**, 1307, 2164). Oxidised with alkaline potassium ferricyanide, it passes into *ethoxy-mustard oil* and *ethoxy-benzo-thiazol* $C_6H_4\langle{}^{N}_{S}\rangle C.OC_2H_5$. In alkalies it dissolves like the phenol-thio-ureas, and makes metallic compounds with silver, mercury, and lead.

Phenyl-imido-thio-carboxylic acid $C_6H_5N:C\langle{}^{OH}_{SH}$ is unknown. Its ethers are formed by the action of alkyl iodides upon the metallic combinations of the phenyl-sulphur-ethanes and upon the free phenyl-sulphur-ethanes. A similar behaviour is shown by the thio-acetanilides and the phenyl-sulpho-ureas. **Ethyl-methyl ester** $C_6H_5N:C\langle{}^{OC_2H_5}_{SCH_3}$, b.p. 260°. **Diethyl ester,** m.p. 30° (A. **207**, 148).

PHENYL-DITHIO-CARBAMINIC ACID DERIVATIVES.—The free acid, precipitated from the potassium salt, decomposes into aniline and SC_2. Its potassium salt, $C_6H_5NHCSSNH_4$, is formed from aniline, CS_2, and aqueous ammonia (*J. pr. Ch.* 2, **65**, 369). For further aryl-dithio-carbaminates, see B. **40**, 2970.

Phenyl-dithio-carbaminic methyl ester, m.p. 87°, and **phenyl-dithio-urethane,** m.p. 60°, formed by heating phenyl-mustard oil with mercaptans, which split again at higher temperatures. They dissolve in alkalies.

Ethyl-phenyl-dithio-urethane $(C_2H_5)C_6H_5NCSSC_2H_5$, m.p. 68°, b.p. 310°, from diphenyl-pseudo-ethyl-thio-urea, with CS_2 at 160°. This compound is very stable, does not dissolve in alkalies, and is not freed from sulphur by HgO, or alkaline lead solutions. On heating with methyl iodide the phenyl-dithio-urethanes, like phenyl-sulphur-ethane, and diphenyl-sulpho-urea, form addition products.

Phenyl-thiuram-sulphide $S(CSNHC_6H_5)_2$, m.p. 137° (B. **24**, 3023).

Methyl-phenyl-thio-carbamine chloride $(CH_3)C_6H_5N.CSCl$, m.p. 35°, from methyl-aniline and thio-phosgene (B. **20**, 1631).

PHENYL-SULPHO-UREAS.—**Phenyl-sulpho-urea,** *sulpho-carbanile-amide* $NH_2CSNHC_6H_5$, m.p. 154°, from phenyl-mustard oil and ammonia,

or from ammonium phenyl-dithio-carbaminate with Pb carbonate (*J. pr. Ch.* 2, **65**, 369). On boiling with silver nitrate it passes into phenyl-urea; with HgO into phenyl cyanamide; with bromine, in chloroform solution, phenyl-thio-urea gives the bromide of a disulphide $C_6H_5N : C(NH_2)SSC(NH_2) : NC_6H_5$, m.p. 128° (B. **34**, 3130); with methyl iodide it combines to form the iodo-hydrate of n-phenyl-methyl-pseudo-thio-urea. With acetic anhydride the unstable **as-phenyl-acetyl-thio-urea,** m.p. 145°, is formed at first, which, on heating above the m.p., is transformed into the symmetrical variety $C_6H_5.NH.CSNH.COCH_3$, m.p. 171° (C. 1902, I. 1300; 1908, I. 1541). These reactions are generally applicable to aromatic thio-ureas.

s-Diphenyl-sulpho-urea, *sulpho-carbanilide* $CS(NHC_6H_5)_2$, m.p. 151°, brilliant colourless flakes, easily soluble in alcohol (B. **19**, 1821). Formed: (1) from phenyl-mustard oil, and aniline, in alcoholic solution; (2) by boiling aniline with CS_2, and withdrawing SH_2. The formation of the urea is greatly favoured by the addition of sulphur or hydrogen peroxide (B. **39**, 4369).

Reactions of sulpho-carbanilide are known in great number:— (1) Iodine converts it into sulpho-carbanile and α-triphenyl-guanidin. (2) Boiling with concentrated HCl splits it up into phenyl-mustard oil, and aniline (B. **16**, 2016). (3) Extraction of sulphur with HgO produces the symmetrical diphenyl-urea. (4) In benzene solution with HgO, carbo-diphenyl-imide is formed. (5) With ammonia, and Pb_2O, we obtain diphenyl-guanidin; with aniline, triphenyl-guanidin; with hydroxylamine, oximido-diphenyl-urea $(C_6H_5NH)_2C : NOH$; with hydrazin hydrate, in the presence of alkalies, amido-diphenyl-guanidin, etc.

Phenyl- and symmetrical diphenyl-sulpho-ureas, dissolved in alkalies, form salts in which the metal adheres to the sulphur (cp. thio-acetanilide).

As to alkyl-phenyl-sulpho-ureas, see B. **17**, 2088; **23**, 815; **26**, 1686. **as-Diphenyl-sulpho-urea,** m.p. 198°, from diphenyl-amine-rhodanide (B. **26**, R. 607). **Triphenyl-thio-urea,** m.p. 152° (B. **17**, 2092). **Tetra-phenyl-thio-urea** $(C_6H_5)_2N.CS.N(C_6H_5)_2$, m.p. 195°, is generated by heating *triphenyl-guanidin* with CS_2 (B. **15**, 1530).

Phenyl-sulpho-hydantoins.—While the product formerly taken for thio- or sulpho-hydantoïn has turned out to be pseudo-hydantoïn, aromatic phenyl-sulpho-hydantoïns have become known (B. **24**, 3278).

Phenyl-α-methyl-sulpho-hydantoin $SC\langle^{N(C_6H_5).CO}_{NH\text{——}CHCH_3}$ or $HSC\langle^{N(C_6H_5).CO}_{N\text{——}CHCH_3}$, m.p. 184°, by melting phenyl-mustard oil and alanin together.

PHENYLATED PSEUDO-SULPHO-UREA DERIVATIVES.—Such compounds are obtained, *e.g.*, from phenyl- and symmetrical diphenyl-sulpho-urea by the action of alkyl iodides and caustic potash, or, better, by heating with alkyl iodides or bromides in alcoholic solution (B. **25**, 48). In the latter case we get the iodo-hydrate of a base which is precipitated by sodium-carbonate solution, and may again add halogen alkyl. On heating with alcoholic potash, the imido-phenyl-carbaminic thio-ester splits off mercaptans.

n-Phenyl-methyl-pseudo-thio-urea, *imido-phenyl-carbaminic thio-*

methyl ester $^{C_6H_5NH}_{NH}\!\!>\!\!CSCH_3$, m.p. 71°. **Sym. diphenyl-pseudo-methyl-thio-urea,** *phenyl-imido-phenyl-carbaminic thio-methyl ester* $^{C_6H_5NH}_{C_6H_5N}\!\!>\!\!C.SCH_3$, m.p. 110°. On heating with dilute sulphuric acid, both yield phenyl-carbaminic thio-methyl ester, which proves the adhesion of the methyl to sulphur. With alcoholic ammonia at 120°, phenyl-guanidin and mercaptan are formed. Heated with CS_2, the diphenyl-pseudo-methyl-thio-urea passes into phenyl-mustard oil and phenyl-dithio-carbaminic ester (B. **15,** 343). Phenyl-pseudo-methyl-thio-urea gives, with acetyl chloride, an as-acetyl derivative, m.p. 86°, which, on heating, passes into the symmetrical form (C. 1902, I. 1300).

With CH_2I_2, $CH_2Br.CH_2Br$, and $CH_2Br.CH_2.CH_2Br$, diphenyl-thio-urea gives cyclic derivatives of pseudo-sulpho-urea (B. **21,** 1872):

$C_6H_5N:C\!<\!^{N(C_6H_5)}_{S}\!\!>\!\!CH_2$ $C_6H_5N:C\!<\!^{N(C_6H_5).CH_2}_{S\text{———}CH_2}$ $C_6H_5N:C\!<\!^{N(C_6H_5).CH_2}_{S—CH_2—CH_2}$.

The ethylene derivative contains the so-called thi-azol ring; the trimethylene derivative, the next higher penthi-azol ring, which is homologous with the thi-azol ring.

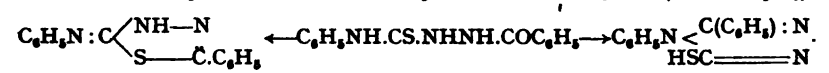
Triphenyl-pseudo-thio-urea $^{(C_6H_5)_2N}_{C_6H_5N}\!\!>\!\!C.S.C_6H_5$, m.p. 185°–188°, by transformation of triphenyl-chloro-carbamidin with sodium-thiophenol (B. **36,** 965).

Pseudo-phenyl-thiohydantoinic acid $HN:C\!<\!^{NHC_6H_5}_{SCH_2CO_2H}$, m.p. 150° (C. 1898, II. 296), and **Pseudo-diphenyl-thiohydantoinic acid** $C_6H_5N:C\!<\!^{NHC_6H_5}_{SCH_2CO_2H}$, formed from phenyl- and diphenyl-thio-urea with chloracetic acid. By rejecting water, these compounds pass into pseudo-hydantoïns: unstable **Pseudo-phenyl-thiohydantoin** $HN:C\!<\!^{N(C_6H_5).CO}_{S\text{———}CH_2}$, m.p. 148°, from **Rhodan-acetanilide** $CNS.CH_2CONHC_6H_5$, m.p. 91°, by heating to 100°, and on further heating it forms a stable isomeric $C_6H_5N:C\!<\!^{NH.CO}_{S—CH_2}$, m.p. 178°; on boiling with HCl, the latter splits up, to form pseudo-phenyl-thiohydantoïnic acid, and, subsequently, forms a mixture of aceto-iso-thiocyanic acid and phenyl-aceto-iso-thiocyanic acid $CO\!<\!^{N(C_6H_5).CO}_{S\text{———}CH_2}$ (C. 1902, II. 792). The latter is also formed by the breaking up of **Pseudo-diphenyl-thiohydantoin** $C_6H_5N:C\!<\!^{N(C_6H_5).CO}_{S\text{———}CH_2}$, m.p. 176°.

HYDROXYLAMINE AND HYDRAZIN DERIVATIVES OF THE PHENYLATED THIO-UREAS.—**Phenyl-hydroxyl-thio-urea** $C_6H_5NHCSNHOH$, m.p. 106°, from hydroxylamine and phenyl-mustard oil, is easily decomposed into water, sulphur, and phenyl cyanamide (B. **24,** 378).

Phenyl-thio-semicarbazide, *phenyl-thiocarbaminic hydrazide* $C_6H_5NH.CS.NH.NH_2$, m.p. 140°, from phenyl-mustard oil and hydrazin hydrate; or from diphenyl-sulpho-urea with hydrazin hydrate in alcoholic solution (B. **33,** 1058). With aldehydes it is transformed into phenyl-thio-semicarbazones. Its acyl derivatives easily yield thio-bi-azolins (*q.v.*) with rejection of water. A peculiar behaviour is shown by the benzoyl derivative, which, when deprived of H_2O by means

of acetyl chloride, yields a phenyl-imido-phenyl-thio-bi-azolin ; or by means of benzoyl chloride, a diphenyl-triazol mercaptan (B. **29**, 2914) :



Phenylated Guanidin Derivatives.—Phenyl-guanidin $NH : C\langle^{NHC_6H_5}_{NH_2}$, m.p. 60°, from cyanamide and aniline chlorohydrate. By an analogous process we obtain **Diphenyl-guanidin,** *melanilin* $NH : C(NHC_6H_5)_2$, m.p. 147°, from cyananilid (p. 106) and aniline chlorohydrate, and also by the action of ClCN upon dry aniline. Both, like guanidin itself, are mono-acid bases. CS_2 decomposes diphenyl-guanidin into diphenyl-sulpho-urea and KSCN.

α-Triphenyl-guanidin $C_6H_5N : C(NHC_6H_5)_2$, m.p. 143°, formed on heating diphenyl-urea or diphenyl-sulpho-urea, by itself, or with copper, to 140°, also by warming the alcoholic solution of diphenyl-sulpho-urea and aniline with $Pb(OH)_2$ (C. 1902, II. 795) or HgO, or by boiling it with iodine solution. CS_2 splits it up into diphenyl-sulpho-urea and phenyl-mustard oil.

β-Triphenyl-guanidin $NH : C\langle^{N(C_6H_5)_2}_{NHC_6H_5}$, m.p. 131°, has been obtained by heating cyano-anilide with diphenyl-amine chlorohydrate. CS_2 breaks it up into diphenyl-amine, phenyl-mustard oil, and hydrogen sulpho-cyanide.

Sym. Tetraphenyl-guanidin $NH : C[N(C_6H_5)_2]_2$, m.p. 130°, by action of CNCl upon diphenyl-amine at 170°.

as-Tetraphenyl-guanidin $C_6H_5N : C\langle^{N(C_6H_5)_2}_{NHC_6H_5}$, m.p. 140°, and **Pentaphenyl-guanidin** $C_6H_5N : C[(NC_6H_5)_2]_2$, m.p. 179°, obtained by transformation of aniline and diphenyl-amine, respectively, with triphenyl-chloro-carbamidin (B. **36**, 964).

Amido-diphenyl-guanidin $C_6H_5N : C(NHC_6H_5)NH.NH_2$, m.p. 99°, formed from diphenyl-thio-urea with hydrazin hydrate in alcoholic alkaline solution (without alkali, phenyl-thio-semicarbazide is formed) ; it is a strong base. With anilines it gives addition products; with carboxylic acids, and with HNO_2, it condenses to triazol and tetrazol derivatives respectively (B. **33**, 1058 ; **35**, 1710, 1716).

Diphenyl-oxyguanidin, *oximido-diphenyl-urea* $HON : C(NHC_6H_5)_2$, m.p. 151°, from diphenyl-thio-urea with alcoholic hydroxylamine solution and PbO (B. **32**, 2238).

PHENYL-BIGUANIDES.—**α-Phenyl-biguanide** $^{NH}_{NH_2}\!\!\rangle C.NH.C\langle^{NH}_{NHC_6H_5}$, chlorohydrate, m.p. 237°, by heating aniline chlorohydrate with dicyano-diamide (C. 1905, I. 730 ; II. 1530). **α-Diphenyl-biguanide** $^{NH}_{NH_2}\!\!\rangle C.NH.C\langle^{NC_6H_5}_{NHC_6H_5}$, m.p. 167°, from sulpho-carbanilide and guanidin (see A. **310**, 335 ; B. **34**, 2594).

G. Phenylated Nitriles and Imides of Carbonic Acid.

Phenyl isocyanate, *carbanile* $C_6H_5N : CO$, b.p. 166°, a liquid with an acrid odour, formed (1) by distillation of oxanilides ; (2) by distillation of carbanilic esters with P_2O_5 (B. **25**, 2578) ; (3) from diazo-benzol

salts by the action of potassium cyanate and copper (B. **25,** 1086); (4) from phenyl-mustard oil $C_6H_5.N:CS$ by heating with HgO to 170° (B. **28,** 1536); (5) by the action of thionyl chloride upon benzo-hydroxamic acid (*q.v.*) in benzene solution (C. 1907, I. 633); (6) by warming benzoyl azide (*q.v.*) or benzoyl chloride and sodium azide, in neutral solvents (B. **42,** 3133, 3359); (7) by the action of HNO_2 upon monophenyl-urea, with excess of HCl (C. 1906, II. 510); (8) by action of phosgene upon aniline, or its chlorohydrate. By methods 6, 7, and 8 a series of substituted carbaniles could also be prepared (C. 1900, I. 30; 1902, II. 554).

Carbanile behaves very similarly to the isocyanic alkyl esters. With water it becomes diphenyl-urea, with alkalies it forms salts of phenyl-carbaminic acid (*J. pr. Ch.* 2, **73,** 177). With alcohols and phenols it combines to form carbanilic esters, a reaction useful for proving the presence of *alcoholic hydroxyls* (B. **18,** 2428, 2606). It reacts similarly with the SH group, and with the hydroxyl group of the aldoximes and ketoximes. With the groups C:O and C:S carbanile does not react (B. **25,** 2578); but it unites with 1, 3-dicarbonyl compounds, like acetyl-acetone, aceto-acetic ester, malonic ester, etc., in the presence of small quantities of alkali, to form C-carbanilide derivatives, *e.g.* $C_6H_5NHCOCH(COCH_3)CO_2R$, which, in contrast with O-carbanilide derivatives, have an acid nature and show the ferric chloride reaction (B. **37,** 4627).

With NH_3 we obtain phenyl-urea. With diazo-amido-compounds $C_6H_5N_2NHR'$ mixed ureas are formed, in which the hydrogen of the NH group is represented by the residue—$CONHC_6H_5$ (B. **22,** 3109). For action upon dicarboxylic acids, see C. 1906, I. 1017; upon oxy-acids, C. 1903, I. 564.

All these phenyl-cyanate reactions, if taking place in the absence of a solvent, usually take place normally without transpositions, and are therefore suitable for determinations of constitution (B. **28,** 2179; **38,** 22). By heating of carbanile with benzene and Al_2Cl_6, we obtain benzoyl anilide (see synthesis of benzoic acid).

o-, m-, p-Tolyl isocyanate $CH_3C_6H_4N:CO$, m.p. 186°, 183°, 187°, by method 7.

Triphenyl isocyanurate $C_3O_3(NC_6H_5)_3$, m.p. 275°, formed (1) by polymerisation of carbanile, on heating with potassium acetate (B. **18,** 3225); (2) by the action of concentrated HCl at 150° upon triphenyl-iso-melamin.

Triphenyl cyanurate $C_3N_3(OC_6H_5)_3$, m.p. 224°, by the action of cyanic or cyanuric chloride upon sodium phenol.

Isocyano-phenyl chloride, *phenyl-imido-carbonyl chloride* $C_6H_5N:CCl_2$, b.p. 209°, a colourless oil, of acrid odour, formed from phenyl isocyanide and chlorine in chloroform solution; also from phenyl-mustard oil and chlorine (B. **26,** 2870). With aniline it passes into α-triphenyl-guanidin (A. **270,** 282).

Phenyl sulpho-cyanide $C_6H_5S.CN$, b.p. 131°, is isomeric with phenyl-mustard oil and *methenyl-amido-thio-phenol* $C_6H_4\langle{}^{S}_{N}\rangle CH$ (see Amido-thio-phenols). Formed by action (1) of HSCN upon diazo-benzol sulphate, and (2) of cyanogen chloride upon lead thio-phenol. It behaves like the alkyl sulpho-cyanic esters.

Phenyl-mustard oil, *sulpho-carbanile, iso-thio-cyanic phenyl ester* $C_6H_5N:CS$, b.p. 222°, is a colourless liquid smelling of mustard oil. Formed (1) from diphenyl-sulpho-urea by splitting off aniline with hot sulphuric acid or concentrated HCl, or, best, with concentrated phosphoric acid (B. **15,** 986); (2) besides triphenyl-guanidin, from diphenyl-sulpho-urea with alcoholic iodine solution; (3) by action of thio-phosgene upon aniline; (4) by action of HNO_2 upon phenyl-sulpho-urea (C. 1906, II. 510).

Heating with copper or zinc dust converts it into benzo-nitrile, the phenol-iso-nitrile first formed transposing into benzo-nitrile at the temperature of reaction. Heated with dry alcohols to 120°, or in alcoholic potash solution, it becomes phenyl-sulphur-ethane (C. 1900, I. 289); with ammonia, aniline, hydrazin, or hydroxylamine it becomes phenyl-sulpho-urea; with chlorine, iso-cyano-phenyl chloride. With sodium-malonic ester it combines to form thio-carbanilino-malonic ester (C. 1908, I. 1929). Combines with aromatic hydrocarbons, phenol ethers, and thio-phenol ethers under the influence of Al chloride to thio-anilides of carboxylic acids (*J. pr. Ch.* 2, **59,** 572).

With alkyl-magnesium iodides (Vol. I.), phenyl-mustard oil combines to form salts which, on decomposition with acids, yield thio-anilides of fatty acids, *e.g.* $NH.CS.CH_3$ (B. **36,** 585). By reduction with zinc and HCl, it is decomposed into aniline and thio-formaldehyde, but by Al amalgam into sulpho-carbanilide and methyl mercaptan (B. **34,** 2033).

PHENYLATED CYANAMIDE DERIVATIVES (cp. Cyanamide, Vol. I.).—**Phenyl-cyanamide,** *cyananilide* $C_6H_5NHCN+\frac{1}{2}H_2O$, m.p. 47°, loses its water of crystallisation in the drying oven, liquefies, and re-forms the hydrate in air. On standing, or heating, it polymerises to triphenyl-iso-melamine. Formed (1) by conducting CNCl into an ether solution of aniline; (2) by heating phenyl-sulpho-urea, with HgO or lead acetate and alkali (B. **18,** 3220). It is easily soluble in alcohol and ether, and combines again with H_2S to form phenyl-sulpho-urea. For substituted cyananilides, see C. 1905, I. 441; 1907, I. 543.

Phenyl-methyl cyanamide $C_6H_5N(CH_3)CN$, m.p. 30°, from cyananilide, ICH_3 and $NaOC_2H_5$ (B. **33,** 1383); or from mono-, or even dimethyl-aniline, with CNBr. The latter process has yielded a number of homologous phenyl-alkyl cyanamides (B. **33,** 2728; **35,** 1279).

Diphenyl cyanamide $(C_6H_5)_2NCN$, m.p. 73°, from as-diphenyl-thio-urea with ammonia, and silver solution (B. **26,** R. 607).

Carbo-diphenyl-imide $C_6H_5N:C:NC_6H_5$, a thick liquid, b.p.$_{30}$ 218°. On distillation, at ordinary pressures, carbo-diphenyl-imide transposes into a polymeric modification melting at 161°, and having triple molecular weight (B. **28,** 1004).

Carbo-diphenyl-imide is formed (1) by action of HgO upon a solution of symmetrical diphenyl-sulpho-urea in benzene; (2) by distillation of α-triphenyl-guanidin; (3) by heating phenyl isocyanate to 180°, with rejection of CO_2 (B. **41,** 1125). With water it combines to form a symmetrical diphenyl-urea; with H_2S, to a symmetrical diphenyl-sulpho-urea; with aniline, to α-triphenyl-guanidin; with phenol, to diphenyl-iso-urea phenyl ether (C. 1909, II. 426). On conducting HCl into a benzene solution of carbo-diphenyl-imide we obtain the compounds $C_6H_5N:CCl.NHC_6H_5$ and $C_6H_5NH.CCl_2.NHC_6H_5$

(B. **28**, R. 778); with malonic ester, and similar bodies, carbo-diphenyl-imide forms substances like $C_6H_5NH.C(NC_6H_5).CH(CO_2C_2H_5)_2$ (B. **32**, 3176). It also combines with aliphatic and thio-aliphatic acids to form compounds like *acetyl-diphenyl-urea* and *acetyl-diphenyl-thio-urea* (*J. pr. Ch.* 2, **64**, 261).

Alkyl-magnesium iodides give Mg compounds, which, with acids, decompose into diphenyl-amidines.

Carbodi-p-tolyl-imide $(C_7H_7N)_2C$, m.p. 57°–59°.

Triphenyl-melamine, *triphenyl-cyanuro-triamide*

$$C_6H_5N : C\langle \begin{matrix} NH.C(NHC_6H_5) \\ NH.C(NHC_6H_5) \end{matrix} \rangle NH,$$

m.p. 228°, by the action of cyanuro-chloride upon aniline, or by heating tri-thia-cyanuric methyl ester with aniline to 250°–300° (B. **18**, 3218).

Hexaphenyl-melamine, $C_3N_3[N(C_6H_5)_2]_3$, m.p. 300°, from cyanuric chloride and diphenyl-amine.

Triphenyl-isomelamine $NH : C\langle \begin{matrix} N(C_6H_5).C(NH) \\ N(C_6H_5).C(NH) \end{matrix} \rangle NC_6H_5$, m.p. 185°, by polymerisation of phenyl cyanamide; also by the action of cyanogen bromide upon aniline. On heating with HCl the NH groups are successively replaced by oxygen, with final formation of isocyanuric triphenyl ester.

Besides the normal and iso-triphenyl-melamines, unsymmetrical triphenyl-melamines are also known (B. **18**, 228).

ANILIDES OF DICARBOXYLIC ACIDS.—Oxalic acid and its homologues, as well as the unsaturated dicarboxylic acids, form anilic acids and dianilides, corresponding to the amino-acids and the diamides. Those dicarboxylic acids capable of forming anhydrides yield also aniles or phenyl-imides corresponding to the imides.

The anilic acids are obtained (1) by partial decomposition of the dianilides; (2) on mixing the ethereal or chloroform solutions of the anhydrides with aniline (B. **20**, 3214); (3) by the breaking down of the aniles. The latter are re-formed from the anilides by treatment with PCl_5 (B. **21**, 957), or with acetyl chloride. They also appear on heating the acids or anhydrides with aniline. A large number of these compounds have been mentioned in the first volume, in connection with their respective acids.

PHENYL-AMINE DERIVATIVES OF OXALIC ACID.—**Oxanilic acid** $C_6H_5NH.CO.CO_2H$, m.p. 150° (see A. **270**, 295, for an isomeric acid, m.p. 210°), is formed by heating oxalic acid and aniline to 140° (B. **23**, 1820), by the action of alcoholic potash upon oxanilide, and when citracon-anilic acid is oxidised with MnO_4K (B. **23**, 747). **Methyl ester,** m.p. 114° (A. **254**, 10); **ethyl ester,** 66°; **chloride,** 82° (B. **23**, 1823).

Oxanilic acid nitrile, *cyano-formanilide* $C_6H_5NHCOCN$, m.p. 120°, prepared by adding hydrocyanic acid to phenyl isocyanate. On heating above its m.p. it decomposes into its constituents. On careful saponification it passes into **phenyl-oxamide** $C_6H_5NHCOCONH_2$, m.p. 224°; by addition of H_2S it becomes **oxanilic acid thio-amide** $C_6H_5NHCOCSNH_2$, m.p. 176° (B. **38**, 2977).

Oxanilide $(CONHC_6H_5)_2$, m.p. 245°, is also obtained from the isomeric **glyoxime-N-phenyl-ether** $C_6H_5N\langle O \rangle CH—CH\langle O \rangle NC_6H_5$, m.p.

183°, by transformation with glacial acetic acid and acetic anhydride. The latter is formed (1) from nitroso-benzol with diazo-methane; (2) from β-phenyl-hydroxylamine with glyoxal or with formaldehyde (B. **30**, 2871; **35**, 1833).

A number of sulphuretted derivatives of oxanilic acid are obtained by action of P_2S_5 upon the corresponding compounds of oxalic acid. They are distinguished by their intense yellow or reddish-yellow colour (B. **37**, 3708).

Thio-oxanilic acid $C_6H_5NHCSCOOH$, m.p. 102°. **Thio-oxanilide** $C_6H_5NHCS.CONHC_6H_5$, m.p. 145°. Both compounds are easily converted into derivatives of benzo-thiazol (*q.v.*).

Thio-oxanilic thio-amide $C_6H_5NHCS.CSNH_2$, m.p. 98°.

Dithio-oxanilide $(CSNHC_6H_5)_2$, m.p. 134°, is also generated by the action of H_2S upon oxanilide chloride (C. 1902, II. 121).

Tetra-p-tolyl-oxamide $[CON[4](C_6H_4[1]CH_3)_2]_2$, m.p. 127°, from p-ditolyl-urea chloride.

Oxanilide dioxime $[C:(NOH)(NHC_6H_5)]_2$, m.p. 215° with decomposition, from *dibromo-glyoxime peroxide*. **Semi-ortho-oxalic-dianilido-methyl ester** $CO_2CH_3.C(NHC_6H_5)_2OCH_3$, and **Phenyl-imido-oxalic dimethyl ester** $CO_2CH_3C:NC_6H_5(OCH_3)$, m.p. 111°, from dichlor-oxalic ester (B. **28**, 60) and aniline. **Phenyl-oxaminic diphenyl-amidine** $C_6H_5NHCO.C\langle^{NHC_6H_5}_{NC_6H_5}$, m.p. 134°, from semi-ortho-oxalic ester and from *oxanile dichloride acid ethyl ester* (A. **184**, 268).

The corresponding nitrile, *carbo-diphenyl-imide-hydrocyanide*, $NC.C(NHC_6H_5):NC_6H_5$, generated from carbo-diphenyl-imide by union with hydrocyanic acid, yields, with yellow Am_2S, a thiamide $NH_2CS.C(NHC_6H_5):NC_6H_5$, which can be easily converted into *isatin anilide* and *indigo*.

o-Nitro-oxanilic acid, m.p. 112°.

o-Dinitro-oxanilide, see A. **209**, 369.

Malon-anilic acid $C_6H_5NHCOCH_2CO_2H$ melts at 132°, with decomposition into CO_2 and acetanilide. It is also formed by a peculiar transposition of sodium acetyl-phenyl-carbaminate from sodium acetanilide with CO_2, on heating to 140° (B. **18**, 1359). With PCl_5 it forms trichloro-quinolin (B. **18**, 2975).

Malon-anilide $CH_2(CONHC_6H_5)_2$, m.p. 223° (B. **17**, 135, 235). **Malonic methyl-anilide** (B. **31**, 1826). **Dithio-malon-anilide** $CH_2(CSNHC_6H_5)_2$, m.p. 149°, from malon-anilide, with P_2S_5 (B. **39**, 3300).

Succin-anilic acid, succin-anile, see Vol. I.: Succinimide.

Fumar-anilic acid, fumar-anilic chloride, fumaric dianilide, malein-anilic acid, malein-anile, dichloro-malein-anile, dichloro-malein-anile dichloride, dichloro-malein-anile-dimethyl ester, dichloro-malein-imidanile, dichloro-malein-dianile, citracon-anilic acid, citracon-anile, itacon-anilic acid, see Vol. I. in connection with the corresponding carboxylic acids.

ANILIDO-CARBOXYLIC ACIDS.—**Anilido-malonic acid** $C_6H_5NH.CH(COOH)_2$ melts at 119°, with rejection of CO_2, and formation of phenyl-glycin. Its esters (methyl, m.p. 68°; ethyl, m.p. 45°) are formed from the bromo-malonic esters, with aniline, and behave like malonic esters in having their C atom alkylated, and in forming addition products with α, β-olefin-carboxylic ester, etc. (see Vol. I.).

On heating to 260°–265° they condense to indoxyl-acetic esters, which can easily be converted into *indigo* (B. **35**, 54). For the effect of nitrous acid, see C. 1902, II. 1318.

For **phenyl-asparagin-anilic acid, phenyl-asparagin-anile, β-anilido-pyro-tartaric acid,** and **pseudo-itacon-anilic acid,** see Amido-succinic acids, Vol. I.

PHENYLATED UREÏDS OF DICARBOXYLIC ACIDS.—**Phenyl-parabanic acid** $CO\langle^{N(C_6H_5)—CO}_{NH———CO}$, m.p. 208°, and **diphenyl-parabanic acid,** m.p. 204°, from the corresponding carbamides with ethoxalic chloride (*J. pr. Ch.* 2, **32**, 20).

Diphenyl-malonyl-urea, *diphenyl-barbituric acid* $CO\langle^{N(C_6H_5).CO}_{N(C_6H_5).CO}\rangle CH_2$, m.p. 238°, formed by the action of malonyl chloride upon carbanilide.

As uric acid is obtained from malonyl-urea (Vol. I.), so from diphenyl-malonyl-urea, through the intermediacy of **diphenyl-violuric acid,** m.p. 227°, we obtain **diphenyl-uramile,** m.p. 195°; **diphenyl-ψ-uric acid,** m.p. 217°; and **1, 3-diphenyl-uric acid,** m.p. above 300° (C. 1907, II. 1065).

ANILINE SUBSTITUTION PRODUCTS.—It is only the aniline derivatives, among the substitution products of the primary phenyl-amines, which deserve particular consideration, for it was with them that the regularities of substitution obtaining among the aromatic amido-bodies were observed, and they were the intermediate stages in numerous instances where constitution was to be determined.

ANILINE HALOIDS.—Formation:—(1) Aniline, like phenol, is more readily substituted than benzene. When chlorine or bromine acts upon the aqueous solutions of aniline salts, the halogen atoms enter the [2, 4, 6]-position. Concerning the additive intermediate products preceding substitution, see A. **346**, 128; B. **38**, 2159. Starting with acetanilide, chlorine and bromine produce first p- and o-mono-substitution products; these are immediately converted into o-p-di-substitution derivatives. If, however, chlorine or bromine be allowed to act upon aniline, in the presence of concentrated sulphuric or hydrochloric acid, m-compounds will be produced. By combining with the strong acids the amido-group acquires a negative character. Concerning further substitutions in meta-substituted anilines, see B. **15**, 1328; C. 1899, II. 1049.

Iodine can substitute the anilines directly; the resulting hydriodic acid combines with the excess of base:

$$2C_6H_5.NH_2+I_2=C_6H_4I.NH_2+C_6H_5.NH_2.HI.$$

(2) The mono-halogen anilines can be readily obtained from the mono-halogen-nitro-benzols, which in turn are derived from the nitro-amido-derivatives. The change is effected through the diazo-bodies.

p-Chloraniline is a stronger base than the o- and m-bodies (B. **10**, 974). It has also been obtained by the electrolytic reduction of nitro-benzol in concentrated hydrochloric acid solution. It is very probable that $C_6H_5.NHCl$ is formed at first, but subsequently rearranges itself into p-chloraniline (B. **29**, 1895; C. **1904**, II. 95).

	[1, 2]-, o-		[1, 3]-, m-		[1, 4]-, p-		
	M.p.	B.p.	M.p.	B.p.	M.p.	B.p.	
$FIC_6H_4NH_2$	..	..	..	..	liquid	188°	(A. **243**, 222)
$ClC_6H_4NH_2$	liquid	207°	liquid	230°	70°	230°	(A. **176**, 27)
$BrC_6H_4NH_2$	31°	229°	18°	251°	66°	..	(B. **8**, 364)
$IC_6H_4NH_2$	56°	..	27°	..	63°	..	(B. **17**, 487)

Of the higher halogen substitution products of aniline we may mention the following :—

From acetanilide :

α-[1 NH_2, 2, 4]-**Dichloraniline,** m.p. 63°, b.p. 245° (B. **7**, 1602).
α-[1 NH_2, 2, 4]-**Dibromaniline,** m.p. 79° (A. **121**, 266).

From the nitro-compounds :

β-[1, 4, 2 NH_2]-**Dichloraniline,** m.p. 54°, b.p. 250° (A. **196**, 215).
β-[1, 4, 2 NH_2]-**Dibromaniline,** m.p. 51° (A. **165**, 180).
[1 NH_2, 2, 6]-**Di-iodaniline,** m.p. 122° (C. 1904, II. 319).
[1 NH_2, 2, 4]-**Di-iodaniline,** m.p. 96° (C. 1904, II. 590).

From aniline with Cl and Br :

[1 NH_2, 2, 4, 6]-**Trichloraniline,** m.p. 77°, b.p. 262° (*J. pr. Ch.* 2, **16**, 449 ; B. **27**, 3151).
[1 NH_2, 2, 4, 6]-**Tribromaniline,** m.p. 119° (B. **16**, 635).
[1 NH_2, 3, 4, 5]-**Tribromaniline,** m.p. 118°–119° (C. 1898, I. 939).
[1 NH_2, 2, 4, 6]-**Tri-iodaniline,** m.p. 184° (C. 1910, I. 526).

The five benzene-hydrogen atoms in aniline can be replaced by chlorine or bromine :

Penta-chloraniline, m.p. 232°. **Penta-bromaniline,** m.p. 222°. Halogen benzols are produced by eliminating the amido-group by means of the diazo-compounds.

For **di-, tri-,** and **tetra-iodanilines** and their transformation products, see B. **34**, 3343.

For further aniline haloids, see C. 1907, II. 1784 ; A. **346**, 160.

NITRANILINES $NO_2C_6H_4NH_2$ are isomeric with diazo-benzolic acid $C_6H_5NHNO_2$. Aniline is strongly attacked by nitric acid, and easily resinified. (1) In order to obtain mono- and di-substitution products, acetanilide is nitrated. The acetyl group protects the amido-group, and p- and o-nitro-acetanilide are first formed, with an excess of nitric acid, chiefly the p-compound ; while with the calculated amount of HNO_3, in glacial acetic acid with addition of acetic anhydride, we obtain chiefly the o-nitro-acetanilide (B. **39**, 3903) But if aniline is nitrogenated in the presence of cold concentrated sulphuric acid, meta-nitraniline is also formed, besides the p- and o-varieties (B. **10**, 1716 ; **17**, 261), and its amount increases with the quantity of sulphuric acid present. There is here the linking of an amido-group and, so to speak, transformation into an acid group, which produces meta-substitution. The three isomers are separated by their basicities. On neutralising their acid solutions, o-nitraniline precipitates, first o-, then p-, and then

m-nitraniline (B. **28,** 1954). In a similar manner the nitro-acetanilides can be separated (B. **39,** 3903).

(2) The nitranilines can also be obtained by heating the nitro-benzol haloids to 150°–180° with alcoholic ammonia; also by heating the nitro-phenol ethers, like $C_6H_4(NO_2).O.C_2H_5$, with aqueous ammonia. In both cases it is only the *para-* and *ortho*-derivatives which react, but not the *meta*-derivatives.

(3) The direct introduction of an amido-group into the o- or p-position, with respect to the nitro-groups present, may be effected by the action of an alcohol-alkaline hydroxylamine solution.

(4) By partial reduction of poly-nitro-compounds.

(5) By heating nitro-amido-benzol-sulphonic acids with HCl to 170° (B. **18,** 294; C. 1905, I. 416).

(6) o- and p-nitraniline are produced by transposition of diazo-benzolic acid:

[1, 2]-, **o-Nitraniline,** m.p. 71°; Acet. m.p. 92°. **o-Nitro-dimethyl-aniline,** see B. **32,** 1066.
[1, 3]-, **m-Nitraniline,** m.p. 114°; Acet. m.p. 142°.
[1, 4]-, **p-Nitraniline,** m.p. 147°; „ m.p. 207°.

The nitro-anilines link the diamido- and dinitro-benzols to the nitro-haloid, amido-haloid, and dihaloid benzols:

$$C_6H_4\langle^{NH_2}_{NH_2} \leftarrow C_6H_4\langle^{NO_2}_{NO_2} \rightarrow C_6H_4\langle^{NO_2}_{NH_2} \rightarrow C_6H_4\langle^{NO_2}_{Br} \rightarrow C_6H_4\langle^{NH_2}_{Br} \rightarrow C_6H_4\langle^{Br}_{Br}.$$

When *ortho-* and *para*-nitranilines (not *meta-*) are boiled with alkalies, they part with NH_3, and are converted into their corresponding nitro-phenols $C_6H_4(NO_2).OH$; the di- and tri-nitranilines react even more readily.

The nitranilines approach in character the acid amides as the number of nitro-groups in them increases.

Ammonia converts the corresponding dinitro-phenols or poly-nitro-haloid-benzols into:

α-[1 NH_2, 2, 4]-**Dinitraniline,** m.p. 182°. β-[1 NH_2, 2, 6]-**Dinitraniline,** m.p. 138°.

[1 NH_2, 2, 4, 6]-**Trinitraniline** $C_6H_2(NO_2)_3.NH_2$, *picramide,* is obtained from picric acid through its ether, or by means of picryl chloride. The latter reacts with ammonia, even in the cold. It forms orange-red needles, m.p. 186°. It forms picric acid when heated with alkalies:

$$C_6H_2(NO_2)_3.NH_2 + KOH = C_6H_2(NO_2)_3.OK + NH_3.$$

Sym. Trinitro-xylidine, m.p. 206°, from trinitro-chloro-xylol and NH_3 (B. **28,** 2047).

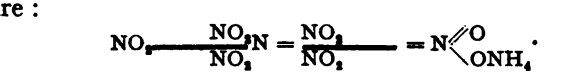
NITRO-DIPHENYL-AMINES are obtained by the transformation of benzol-nitro-haloids with aniline, or of the nitranilines with bromo-benzols and addition of copper bronze or copper iodide. o-Nitro-bromo-benzol and the polynitro-halogen-benzols react with aniline even without a catalyst. In a similar manner the aryl-sulphonic esters of o-nitro-phenol, and its derivatives, yield nitro-diphenyl-amines with aniline (B. **41,** 1870). Numerous nitro-diphenyl-amines have also been obtained by nitrogenating nitroso- or benzoyl-diphenyl-

amine, and breaking up the resulting compounds with dilute SO_4H_2 (C. 1906, I. 28).

The nitro-diphenyl-amines are pale-yellow compounds. They yield dark-red alkali salts, with a stability increasing with the number of nitro-groups they contain.

Hexanitro-diphenyl-amine dissolves in aqueous alkalies, with a purple colour. Its ammonium salt is a brick-red powder. Before the introduction of the azo-dyes, it was used under the name of "aurantia" for dyeing wool and silk. At present it is only used for making photographic colour-filters. The corresponding salt of penta-nitro-diphenyl-amines possesses no dyeing power.

These strongly coloured alkali salts probably possess a quinoid structure :



The nitro-diphenyl-amines probably therefore belong to the class of pseudo-acids (Vol. I.). They form two series of alkyl derivatives : pale-yellow, stable nitrogen ethers corresponding to the free nitro-phenyl-amines ; and dark-violet, unstable oxygen esters corresponding to the dark-coloured alkali salts, and possessing, like the latter, a quinoid structure (aci-nitro-derivatives) :

I. $(NO_2)_2C_6H_2.N(CH_3)C_6H_3(NO_2)_2$ Pale yellow.

II. $(NO_2)_2C_6H_2N : C_6H_3(NO_2)_2 : NOOCH_3$ Deep violet.

o-, m-, and p-Nitro-diphenyl-amine $NO_2C_6H_4NHC_6H_5$, m.p. 75°, 112°, 132° (B. **15**, 826 ; **22**, 903 ; **40**, 4545).

o, o-, p, p-, and o, p-Dinitro-diphenyl-amine $NO_2C_6H_4NHC_6H_4NO_2$, m.p. 167°, 214°, 219° (B. **15**, 826).

[2, 4, 6] - Trinitro - phenyl - phenyl - amine, m.p. 175°, from picryl chloride (B. **8**, 126). **Trinitro-xylyl-phenyl-amine,** m.p. 175° (B. **28**, 2047). Similar compounds, see B. **33**, 594 ; C. 1898, II. 342.

Pentanitro-diphenyl-amine, m.p. 194°. **Hexanitro-diphenyl-amine,** m.p. 238°.

N-Methyl-2, 4-dinitro-diphenyl-amine $C_6H_5N(CH_3)C_6H_3(NO_2)_2$, m.p. 167°, from 1, 2, 4-chloro-dinitro-benzol and methyl-aniline, gives, on further nitrogenation, **N - methyl - hexanitro - diphenyl - amine,** m.p. 236°, yellow flakes. The isomeric **o-methyl-aci-hexanitro-diphenyl-amine,** in violet-black crystals decomposing at 141°, is obtained by the action of ICH_3 upon the silver salt of hexanitro-diphenyl-amine. Traces of alcoholic HCl rapidly saponify the ester. But acetyl chloride gives, with the silver salt, an **N-acetyl-hexanitro-diphenyl-amine,** pale-yellow crystals melting at 240° (B. **41**, 1745).

p-Nitro-phenyl-amine $NO_2C_6H_4N(C_6H_5)_2$, m.p. 144°, from p-nitro-iodo-benzol and diphenyl-amine, in presence of copper bronze (B. **41**, 3511).

H. p-Nitroso-Derivatives of the Primary, Secondary, and Tertiary Aromatic Amines.

Formation.—(1) When the nitrosamines of monomethyl-aniline or diphenyl-amine are treated with alcoholic hydrochloric acid, they rearrange themselves into p-nitroso-compounds (B. **19**, 2991). (2) The p-nitroso-bodies are also produced when nitrous acid acts upon

the tertiary dialkyl-anilines, or sodium nitrite upon their hydrochlorides (Baeyer and Caro, B. **7**, 963). (3) When the nitroso-phenols are fused with ammonium acetate and ammonium chloride, they yield p-nitroso-anilines (B. **21**, 729).

Behaviour.—When the p-nitroso-derivatives of the secondary and tertiary aromatic amines are heated with caustic soda, they break down into sodium nitroso-phenate and alkylamines (I. 163). Most chemists consider the nitroso-phenols to be the monoximes of the paraquinones. And in connection with this mode of formulation of the nitroso-phenols, many are disposed to view the p-nitroso-derivatives, of the secondary and tertiary aromatic amines, as quinine derivatives :

$C_6H_4\{^{[1]:O}_{[4]:O}$	$C_6H_4\{^{[1]:N.OH}_{[4]:O}$	$C_6H_4\{^{[1]:N=(CH_3)_2}_{[4]:N>O}$
p-Quinine.	p-Quinone-monoxime Nitroso-phenol.	p-Nitroso-dimethyl-aniline.

p-Nitroso-aniline $NO[4]C_6H_4[1]NH_2$, m.p. 174°, crystallises in steel-blue needles (B. **21**, 729 ; **28**, R. 735).

p-Nitroso-monomethyl-aniline $NO[4]C_6H_4[1]NHCH_3$ forms blue lustrous flakes, and melts at 118° C. It is soluble in dilute sodium hydroxide, and is again liberated from its solution by carbon dioxide.

When heated with sodium hydroxide, p-nitroso-methyl-aniline is decomposed into sodium nitroso-phenate and methyl-aniline.

p-Nitroso-monoethyl-aniline, m.p. 78°.

o-, m-, and p-Nitroso-acetanilide $NOC_6H_4NHCOCH_3$, m.p. 107°, 111°, 173°, by oxidation of the three mono-acetyl-phenylene-diamines with monopersulphonic acid. The p-nitroso-acetanilide exists in a grey and a colourless modification, m.p. 173° and 181° (C. 1908, I. 2027).

p-Nitroso-dimethyl-aniline $NO[4]C_6H_4[1]N(CH_3)_2$, m.p. 85°, consists of large green flakes. Potassium permanganate and ferrocyanide of potassium oxidise it to p-nitro-dimethyl-aniline. Upon reduction it yields p-amido-dimethyl-aniline, which is so important in the dye manufacture. Sodium hydroxide resolves it into nitroso-phenol and dimethyl-aniline. Its hydrochloride dissolves with difficulty in cold water.

p-Nitroso-diethyl-aniline, m.p. 84°.

p-Nitroso-diphenyl-amine, m.p. 143°, consists of green plates, and is produced when hydrochloric acid gas acts upon diphenyl-nitros-amine. Dissolves in concentrated aqueous alkalies with formation of dark-brown alkali salts, derivable from the anile of quinone-monoxime $C_6H_5N : C_6H_4 : NOH$ (B. **20**, 1252 ; **21**, R. 227).

5*a*. Diamines.

Formation.—The aromatic diamines, whose amido-groups are attached to the benzene nucleus, are formed (1) by the reduction of the three dinitro-benzols or nitro-anilines with tin and hydrochloric acid ; (2) the monamines can be converted into the diamines by first changing them to amido-azo-compounds, and then decomposing the latter by reduction :

$$C_6H_5N{=}N[4]C_6H_4[1]NH_2+4H=C_6H_5NH_2+NH_2[4]C_6H_4[1]NH_2.$$

(3) They can be obtained, also, from the diamido-benzoic acids, by the loss of carbon dioxide, when they are treated with baryta. This reaction has become of particular importance in ascertaining the constitution of the three phenylene-diamines. (4) Phenylated diamido-benzols are formed by the *semidin* transposition of hydrazo-benzols; thus, o-amido-ditolyl-amine is formed from hydrazo-toluol. (5) Diphenylated diamido-benzols $C_6H_4(NH.C_6H_5)_2$ are produced when dioxy-benzols—*e.g.* resorcinol and hydroquinone—are treated with aniline and $CaCl_2$ or $ZnCl_2$.

Properties.—The diamines are colourless solids volatilising without decomposition, but on exposure to the air they become coloured. They are di-acid bases, forming well-defined salts. Ferric chloride imparts an intense red colour to their solution. The amide hydrogen atoms can be replaced in the same manner as in the monamines.

Diamido-benzols, or phenylene-diamines, $C_6H_4(NH_2)_2$. The o-body is derived from o-nitraniline by reduction with caustic soda and zinc dust (B. **28,** 2947). The m-derivative is most easily accessible through m-dinitro-benzol. The p-compound is obtained by the decomposition of amido-azo-benzol, or by heating p-dichloro-benzol with NH_3 in presence of copper sulphate (*Z. f. Ch.* 1866, 136; C. 1908, II. 1221).

[1, 2]-,	o-Phenylene-diamine,	m.p. 102°,	b.p. 252°
[1, 3]-,	m-Phenylene-diamine,	,, 63°,	,, 267°
[1, 4]-,	p-Phenylene-diamine,	,, 147°,	,, 267°.

o-Phenylene-diamine is coloured red, in hydrochloric acid solution, by ferric chloride, with the production of diamido-phenazine hydrochloride (B. **27,** 2782). Oxidation with PCO_2 or Ag_2O gives o-quinone-di-imine, which immediately polymerises to O_2-diamido-benzol. In the table (see below), showing the numerous o-condensations of which the o-diamines are capable, it is o-phenylene-diamine which appears most frequently as the example.

o-Amido-phenyl-urethane melts at 86°.

o-Amido-diphenyl-aniline, b.p. 217° (B. **32,** 1903). 4, 6-Dinitro-o-phenylene-diamine, m.p. 215°, deep-red needles, by reduction of picramide with alcoholic Am_2S (B. **41,** 3093).

m-Phenylene-diamine with nitrous acid becomes *triamido-diazo-benzol,* or *Bismarck brown.* It imparts an intense yellow colour to a very dilute solution of nitrous acid, and can therefore be used for the colorimetric estimation of the latter in water (B. **14,** 1015); if the nitrite solution is allowed to flow quickly into the hydrochloric solution of the m-phenylene-diamine, we obtain, besides Bismarck brown, **1, 2, 4-Nitroso-m-phenylene-diamine** $NOC_6H_3(NH_2)_2$, garnet-red flakes of m.p. 210° (B. **37,** 2276). Concerning the action of $COCl_2$, CS_2, and oxalic ester, cp. B. **7,** 1263; **21,** R. 521; **24,** 2113; **36,** 411.

Tetramethyl-m-phenylene-diamine, b.p. 267° (B. **30,** 3110). **Tetraphenyl-phenylene-diamines** $C_6H_4[N(C_6H_5)_2]_2$ are produced from the dichloro-benzols by heating with potassium diphenyl-amine (B. **32,** 1912). **m-Phenylene-carbyl-amine** $C_6H_4[1, 3](N : C)_2$ is transposed to isophthalic nitrile by heating (C. 1902, I. 463).

o-Nitro- and **o-Amido-phenyl-m-phenylene-diamine** $NH_2[2]C_6H_4.NH.C_6H_4[3]NH_2$, see B. **34,** 3089. **4-Nitro-m-phenylene-diamine,** see

C. 1906, I. 517. **2, 4-Dinitro-m-phenylene-diamine,** m.p. 254° (B. **89,** 2538).

p-Phenylene-diamine oxidises in air to the dark garnet-red crystals of **Tetra-amido-diphenyl-p-azo-phenylene** $C_6H_4\begin{cases}[1]N[1]C_6H_3[2,5](NH_2)_2\\[4]N[1]C_6H_3[2,5](NH_2)_2\end{cases}$ m.p. 231° with decomposition (B. **27,** 480). By Ag_2O it is turned into *quinone di-imine* (*q.v.*), by MnO_2 and sulphuric acid into *quinone* (*q.v.*), by chloride of lime into *quinone dichlorimine* (*q.v.*).

p-Amido-dimethyl-aniline $NH_2[4]C_6H_4[1]N(CH_3)_2$, m.p. 41°, b.p. 257°, is obtained by reduction of p-nitroso- or p-nitro-dimethyl-aniline, or by splitting up **helianthin** or p-dimethyl-amido-azo-benzol (B. **16,** 2235). In acid solution it gives with SH_2 and ferric chloride a dark-blue colour—*methylene blue* (*q.v.*)—and therefore is used as a sensitive reagent for SH_2. **N, N¹-dimethyl-p-phenylene-diamine** $CH_3NH[1]C_6H_4[4]NHCH_3$, m.p. 53°, b.p.$_{17}$ 150°, is oxidised by Ag_2O to *quinone dimethyl-imine* (B. **88,** 2248).

Thionyl- and **formyl-p-amido-dimethyl-aniline,** see B. **27,** 602; **31,** 2179. **p-Phenylene-dicarbyl-amine** $(C_6H_4)[1,4](N:C)_2$ yields, on heating, terephthalic acid nitrile (C. 1902, I. 463). **Nitro-p-phenylene-diamine,** m.p. 135°, lustrous green needles, from [1, 2, 4]-dinitraniline (B. **28,** 1707; **29,** 2284).

DIAMIDO-TOLUOLS, TOLUYLENE-DIAMINES.—All the six isomers predicted by theory are known:

1. [1 CH_3, 2, 3]-Toluylene-diamine, m.p. 61°, b.p. 255° (A. **228,** 243)
2. [1 CH_3, 3, 4]-Toluylene-diamine, ,, 88°, ,, 265°
3. [1 CH_3, 2, 4]-Toluylene-diamine, ,, 99°, ,, 280°
4. [1 CH_3, 2, 6]-Toluylene-diamine, ,, 103°, (B. **17,** 1959)
5. [1 CH_3, 3, 5]-Toluylene-diamine, liquid, ,, 284° (A. **217,** 200)
6. [1 CH_3, 2, 5]-Toluylene-diamine, m.p. 64°, ,, 273°.

[1, 3, 4]-Toluylene-diamine is the most accessible o-diamine. It is prepared from p-aceto-toluidin:

$$C_6H_4\begin{cases}[1]CH_3\\[4]NH.COCH_3\end{cases}\longrightarrow C_6H_3\begin{cases}[1]CH_3\\[3]NO_2\\[4]NHCOCH_3\end{cases}\longrightarrow C_6H_3\begin{cases}[1]CH_3\\[3]NO_2\\[4]NH_2\end{cases}\longrightarrow C_6H_3\begin{cases}[1]CH_3\\[3]NH_2\\[4]NH_2\end{cases}$$

1, 2, 4-Toluylene-diamine is the fundamental body for the preparation of *toluylene red* (*q.v.*).

Xylylene-diamine.—The eleven theoretically possible diamido-xylols have all been obtained, and four of them are derivable from o-phenylene-diamine: $(NH_2)_2[1,2](CH_3)_2[3,4]$, m.p. 89°; -[4, 5]-, m.p. 126°; -[3, 5]-, m.p. 78°; -[3, 6]-, m.p. 75°.

Four derivatives from m-phenylene-diamine: $(NH_2)_2[1,3](CH_3)_2$ [4, 5]-, m.p. 67°; -[2, 4]-, m.p. 66°; -[4, 6]-, m.p. 105°; -[2, 5]-, m.p. 103°; and

Three derivatives from p-phenylene-diamine: $(NH_2)_2[1,4](CH_3)_2$ [2, 3]-, m.p. 116°; -[2, 6]-, m.p. 104°; -[2, 5]-, m.p. 150° (B. **35,** 636).

[1, 2, 3, 5, 6]-o-Diamido-pseudo-cumol, m.p. 90°; **p-Diamido-pseudo-cumol,** m.p. 78° (B. **24,** 1647). **Diamido-mesitylene,** m.p. 90° (A. **141,** 134; **179,** 176, etc.).

In the phenylene-diamines with a methylated nucleus, the amidyl in para-position to a methyl is more easily acidulated than the o- and m-position amidyls (B. **35,** 681). Concerning the influence of nucleus-

alkylene upon the alkylation of the phenylene-diamines at the nitrogen, see C. 1902, I. 1279.

p-Amido-diphenyl-amine $NH_2[4]C_6H_4[1]NHC_6H_5$, m.p. 75°, by reduction of p-nitroso-diphenyl-amine with $(NH_4)_2S$. It also forms during the electrolytic reduction of nitro-benzol in hydrofluosilicic acid solution. Ferric chloride oxidises it to emeraldin (*q.v.*) (B. **40**, 289).

p_2-Diamido-diphenyl-amine, m.p. 158°, by semidin-transposition of p-amido-hydrazo-benzol (C. 1906, I. 232).

p-Amido-triphenyl-amine $NH_2[4]C_6H_4[1]N(C_6H_5)_2$, m.p. 145°–148°, by reduction of the corresponding nitro-compound. A **p-Chloranilino-triphenyl-amine**, m.p. 77°–81°, is formed by a complex reaction in the breaking up of tetraphenyl-hydrazin with HCl (B. **41**, 3507).

The Condensations of the o-Diamines.

The o-diamines possess the power in a remarkable degree of forming condensation products. These usually consist of ring-systems containing five or six atoms, and will be discussed in connection with the heterocyclic carbon derivatives. The m- and p-diamines do not possess this power. The condensation occurs in that hydrogen atoms of both amido-groups of an o-diamine are replaced by polyvalent atomic groups. Frequently, when this occurs, the nitrogen atoms occupying the o-position unite with one another.

1. Sulphur dioxide and selenium dioxide convert the o-diamines into *piazo-thiols* (*q.v.*) and *piazo-selenols* (*q.v.*).

2. Nitrous acid produces *azimides* (*q.v.*).

3. The *cyclic amidines* are directly produced from the o-diamines on heating them with acids, their chlorides and anhydrides, as well as with aldehydes. *Anhydro-bases* or *aldehydins* (Ladenburg). These are substances nearly related to the *glyoxalins* or *imidazols*, and will be treated later in connection with these. Such condensations have been observed also in the reduction of acidylated o-nitro-amido-compounds (Hobrecker).

4. *Cyclic ureas* and *thio-urea derivatives* are formed from $COCl_2$ and $SCCl_2$ or CS_2, also by condensation with urea and thio-urea, as well as with ammonium sulpho-cyanide.

5. *Cyclic guanidin derivatives* are obtained by means of carbo-di-imides and phenyl-mustard oils.

6. A very interesting condensation of the o-diamines is that with glyoxal and other α-dicarbonyl derivatives, as well as with grape-sugar, when *quinoxalins* result, with rejection of water (Hinsberg) (I. 321).

Related six-membered rings are produced :

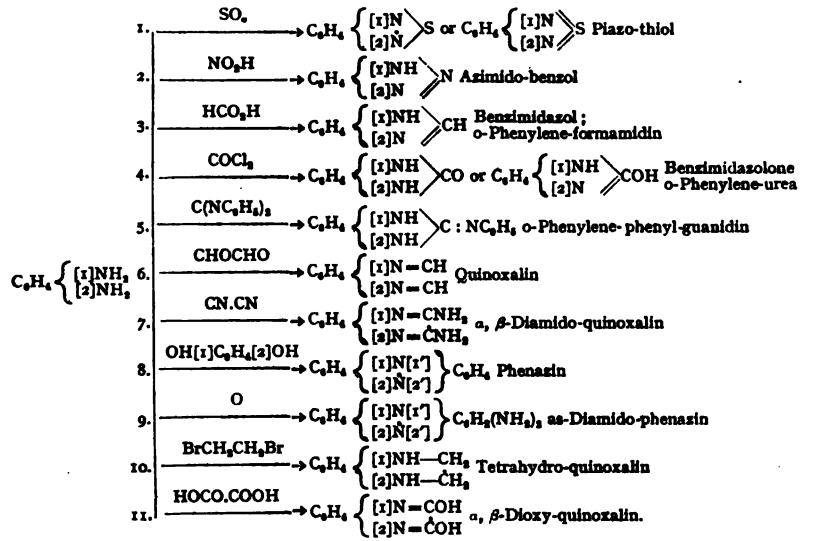
7. When o-diamines condense with cyanogen ;

8. By condensation with o-dioxyl-benzol.

9. *Unsym. diamido-phenazin* is produced by the oxidation of o-phenylene-diamine.

10. Dibenzol-sulphone derivatives of o-phenylene-diamine condense with alkylene dihaloids—*e.g.* methylene iodide, ethylene bromide, trimethylene bromide. The products are cyclic diamines, from which the corresponding *phenylene-alkylene-diamines* are obtained by the splitting off of the benzol-sulphone groups (B. **28**, R. 756).

11. The o-phenylene-diamines condense also with oxalic acid, and the homologous paraffin-dicarboxylic acids, as well as o-phthalic acid, to rings of a higher number of members (A. **327**, 9).



The *o-amido-phenols*, the *o-amido-thio-phenols*, and the *o-dioxy-benzols* show condensations similar to those observed with the o-diamines.

Differences between the o-, m-, and p-Diamines.

1. The *para*-diamines are capable of yielding various dyestuffs. Mixed with primary amines (or phenols) and oxidised at the ordinary temperature, they are converted into *indoamine* and *indophenol* dyestuffs; at higher temperatures the so-called *safranins* are produced. When oxidised with ferric chloride in the presence of H_2S, the para-diamines, containing a free NH_2 group, yield sulphurised dyes of thio-diphenyl-amine (Lauth's dyestuffs). Manganese dioxide and sulphuric acid oxidise the p-diamines to quinones, recognisable by their odour. Ferric chloride (B. **17**, R. 431) imparts colour to the diamines. See above, o-Phenylene-diamine.

2. The *ortho*-diamines, when acted upon by nitrous acid, yield azimido-compounds, *e.g. azimido-benzol.* The *meta*-diamines, on the contrary, yield yellow-brown azo-dyes, of the type of phenylene brown. Test for nitrous acid (B. **11**, 624, 627). In every acid solution, and when there is an excess of acid (nitrous), the meta-diamines form bis-diazo-derivatives. Nitrous acid (or $NaNO_2$) converts the para-diamines (their salts) into bis-diazo-compounds.

3. When the chlorohydrates of the three isomerides are digested with ammonium sulphocyanide, disulphocyanides, like $C_6H_4\langle^{NH_2.HSCN}_{NH_2.HSCN'}$ are produced. On heating these to 120° we discover that the ortho-diamines are changed to cyclic sulpho-ureas

$C_6H_4\langle^{NH}_{NH}\rangle CS$. These are not desulphurised by digestion with an alkaline lead solution; while the derivatives, obtained from the meta- and para-diamines, are immediately blackened by the alkaline lead solution (reaction of Lellmann, B. **18,** R. 326).

4. The diamines unite in a similar manner with the mustard oils. If these products be fused, those from the ortho-diamines decompose into cyclic phenylene-sulpho-urea and dialkyl-sulpho-ureas; the fused mass soon becomes crystalline. The meta-diamine derivatives melt without decomposition, while those of the para-, after fusion, are completely broken up (B. **18,** R. 327; **19,** 808).

5. The o-diamines show a series of other condensation reactions, which have been tabulated above; and as the m- and p-diamines behave differently in these transpositions, they will answer for the distinction of the o-derivatives from the other two classes. The behaviour towards phenanthraquinone is used for the detection of the o-diamines. A more delicate test is that with *croconic acid* (B. **19,** 2727). Both tests are based upon the formation of quinoxalin derivatives.

Triamines.—The three triamido-benzols possible theoretically are known, although the symmetrical body only in the form of its salts.

The adjacent [1, 2, 3] is obtained from triamido-benzoic acid (from chrysanisic acid), m.p. 103°, b.p. 330° (A. **163,** 23). The unsymmetrical [1, 2, 4], m.p. 132°, b.p. 340°, is obtained by the decomposition of *chrysoïdine* (B. **10,** 659; **15,** 2196), or diamido-azo-benzol, and from the corresponding nitro-amido-derivatives (B. **19,** 1253). When oxidised by air it changes to a *eurhodine* dyestuff (B. **22,** 856). [1 CH_3, 2, 3, 4]-**Triamido-toluol** (B. **14,** 2657).

Triamido-mesitylene, m.p. 118°, see C. 1898, II. 539. Di-, tetra-, and hexamethylated triamines, see B. **29,** 1053; **30,** 3110.

Tetramines.—**v-, [1, 2, 3, 4]-Tetra-amido-benzol** is obtained by the reduction of diquinol tetroxime (B. **22,** 1649). The symmetrical (1, 2, 4, 5) variety is formed by the reduction of dinitro-m-phenylene-diamine. It exhibits all the reactions of the ortho- and para-diamines (B. **22,** 440).

Asym. [1, 2, 3, 5]-tetramido-benzol, from tetra-nitro-benzol, see B. **34,** 57.

Pentamines. — **Penta-amido-benzol,** from trinitro-m-phenylene-diamine.

Penta-amido-toluene $CH_3.C_6(NH_2)_5$ is formed from trinitro-s-toluylene-diamine (B. **26,** 2304).

As the number of amido-groups increases the polyamines become more unstable.

In the sym. triamido-benzols the NH_2 groups may be replaced by OH groups, by heating with HCl; sym. triamido-benzol becomes phloro-glucin (M. **21,** 20; **22,** 983).

6. Phenyl-Nitrosamines.

Nitroso-compounds are obtained when potassium nitrite acts upon the hydrochlorides of secondary aromatic bases. This procedure is similar to that employed with the aliphatic nitrosamines. It is a reaction which can be used to distinguish, and separate, secondary

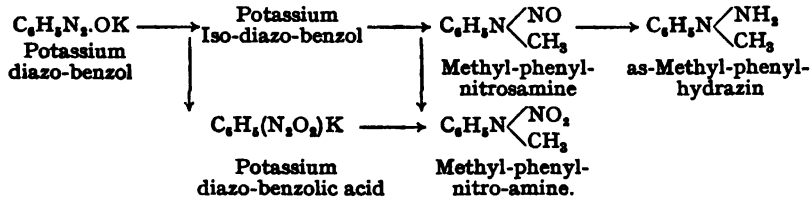
from primary and tertiary bases, as the nitrosamines are precipitated, as oils, from the acid solution of a mixture of bases. The phenyl-nitrosamines in alcoholic or ethereal solution, when treated with hydrochloric acid gas, pass into p-nitroso-anilines :

$$C_6H_5N\begin{matrix}CH_3\\NO\end{matrix} \longrightarrow NO[4]C_6H_4[1]NHCH_3$$

Methyl-phenyl-nitrosamine p-Nitroso-monomethyl-aniline.

They change into hydrazins upon reduction, or break down into ammonia, and the original secondary bases. They are volatile with steam (B. **10,** 329 ; **22,** 1006 ; A. **190,** 151), but decompose upon dry distillation.

The nitrosamines are not only intimately related to the secondary amines and hydrazins, but also to the diazo-compounds. Potassium diazo-benzol may be readily rearranged into potassium iso-diazo-benzol, which yields phenyl-methyl-nitrosamine with methyl iodide. Unsym. phenyl-methyl-hydrazin results from the reduction of phenyl-methyl-nitrosamine. Potassium diazo-benzolate is formed by the oxidation of potassium iso-diazo-benzol. The latter, and methyl iodide, combine to phenyl-methyl-nitramine, which can be reduced to phenyl-methyl-nitrosamine, and unsym. phenyl-methyl-hydrazin. These genetic relations are indicated in the following diagram :



Phenyl-methyl-nitrosamine $C_6H_5N(CH_3)NO$, m.p. 12°–15° (B. **27,** 365, footnote), also from nitroso-phenyl-glycin $C_6H_5N(NO)CH_2COOH$, on boiling with water (B. **32,** 247). The methyl group is replaced by potassium when the substance is fused with caustic potash ; potassium iso-diazo-benzol results. In the cold, phenyl-methyl-nitrosamine forms in HCl, in alcohol, a chlorohydrate $[C_6H_5N(NO)CH_3]HCl$, which, on boiling or heating, is transposed into the isomeric p-nitroso-methyl-aniline (B. **35,** 2975).

Phenyl-ethyl-nitrosamine $C_6H_5N(C_2H_5)NO$ is a yellow oil, with an odour like that of bitter almond oil (B. **7,** 218).

Diphenyl-nitrosamine $(C_6H_5)_2NNO$, m.p. 66°, consists of pale-yellow plates. It dissolves in concentrated sulphuric acid with a dark-blue colour.

For other aromatic nitrosamines, see B. **33,** 100.

NITROSANILIDES.—These bodies are even more closely allied to the diazo-compounds than are the phenyl-alkyl-nitrosamines. They are formed (1) from the anilides in glacial acetic acid solution with nitrous acid ; (2) from the diazo-alkali salts (normal and iso-) with acid chlorides in alkaline solution. Gaseous HCl breaks them up again into anilides and nitrosile chloride NOCl, and the anilides are always restored by reduction also ; alkalies, on the other hand, split off the

acidyl group even at low temperatures, diazo-alkali salts being formed. With potassium sulphite, nitroso-acetanilide forms benzol-diazo-sulphonic acid and phenyl-hydrazin-disulphonic acid. With benzene, nitrous acetanilide yields diphenyl with evolution of nitrogen (B. **30,** 366; A. **325,** 226).

Nitroso-formanilide $C_6H_5N(NO)CHO$, m.p. 39°; **Nitroso-acetanilide** $C_6H_5N(NO)COCH_3$, m.p. 40°; **p-Bromo-nitroso-acetanilide,** yellow needles, exploding at 88°. **Nitroso-phenyl-urea** $C_6H_5N(NO)CO.NHC_6H_5$, m.p. 82° with decomposition, behaves like the nitroso-anilides.

7. Phenyl-Nitramines.

Diazo-benzolic acid, *nitranilide, phenyl-nitramine* $C_6H_5NH.NO_2$ or $C_6H_5N:NOOH$, m.p. 46°, colourless crystals, formed: (1) by oxidation of normal diazo- and iso-diazo-potassium-benzol with potassium ferricyanide or permanganate (B. **28,** R. 82), besides the isomeric nitroso-phenyl-hydroxylamine $C_6H_5N(NO)OH$ (B. **42,** 3568); (2) by nitrogenation of aniline by means of nitrogen pentoxide (B. **27,** 584; cp. **29,** 1015; A. **311,** 91); (3) by the action of sodium upon an etheric solution of aniline and ethyl nitrate (C. 1905, II. 894); (4) by decomposition of diazo-benzol perbromide with alkalies, besides nitroso-benzol (B. **27,** 1273; **28,** R. 31); (5) from nitrite chloride, and aniline (B. **27,** 668); (6) from aniline nitrate and acetic oxyhydride, with splitting off, as in the case of acetanilide, from aniline acetate (A. **311,** 99). A number of substituted diazo-benzolic acids have been prepared by the above methods.

Properties and Behaviour.—In the light, on heating, and in contact with mineral acids, diazo-benzolic acid is transformed into a mixture of o- and p-nitraniline, with which it is isomeric. It is probable that, during nitrogenation of aniline, diazo-benzolic acid occurs as an intermediate product. By reduction with sodium amalgam it passes into sodium-iso-diazo-benzol, and the latter easily into phenyl-hydrazin (B. **27,** 1181). With zinc and acetic acid it yields diazo-benzol. It forms salts: a potassium salt $C_6H_5H_2O_2K$, and a sodium salt of brilliant white flakes. With ICH_3 the sodium salt gives the *a*-methyl ester, **Phenyl-methyl-nitramine** $C_6H_5N\langle^{CH_3}_{NO_2}$, m.p. 39°, which, with sulphuric acid, changes into o- and p-nitro-methyl-aniline, yields methyl-aniline on heating with KHO, and may be reduced to methyl-phenyl-nitrosamine, unsym. methyl-phenyl-hydrazin, and monomethyl-aniline. With methyl iodide the silver salt gives ***β*-Diazo-benzolic methyl ester** $C_6H_5N:NOOCH_3$, a yellowish-brown oil, smelling of heliotrope (B. **27,** 359; cp. B. **31,** 177, 574).

Homologous Diazo-benzolic Acids.—The symmetrical tri-substituted phenyl-nitramines in which the o- and p-positions, with reference to the amido-group, are occupied, do not undergo the transposition into nitraniline. They are stable in the presence of mineral acids, and may therefore be obtained by direct nitrogenation of the corresponding anilines with concentrated NO_3H.

o-Diazo-toluolic acid, a colourless oil. **p-Diazo-toluolic acid,** m.p. 52°. **Diazo-pseudo-cumolic acid,** m.p. 87°. **o-, m-, p-Nitro-diazo-benzolic acid,** m.p. 65°, 86°, 111° (B. **28,** 399). **Dinitro-p-tolyl-methyl-**

nitramine $(NO_2)_2C_6H_2(CH_3).N(CH_3)NO_2$, m.p. 138°, is obtained by the action of nitric acid upon dimethyl-p-toluidin (B. **29**, 1015).

2, 4, 6-Trichloro-phenyl-nitramine, m.p. 135°. **2, 4, 6-Tribromo-phenyl-nitramine**, m.p. 144° (C. 1905, I. 1231). **2, 4-Dinitro-phenyl-nitramine**, m.p. 101° with decomposition, by the action of concentrated nitric acid upon o- and p-nitraniline or 2, 4-dinitraniline (A. **339**, 229).

2, 4, 6-Trinitro-phenyl-nitramine, extremely explosive, generated as a by-product during nitrogenation of aniline (B. **41**, 3094; **42**, 2959).

8. Diazo-compounds.

The aromatic diazo-derivatives, because of their ready conversion into the most varied substitution products of the aromatic hydrocarbons, and as intermediate steps in the formation of azo-dyes, are equally important both from a scientific and technical standpoint.

The behaviour of the primary aliphatic amines towards nitrous acid was particularly emphasised. As is known, the amido-group can, by this means, be replaced by hydroxyl; it is a change corresponding to that of ammonia itself by nitrous acid into nitrogen and water:

$$NH_3+NOOH=H_2O+N_2+H_2O$$
$$C_2H_5NH_2+NOOH=C_2H_5OH+N_2+H_2O.$$

Among the nitrogen-containing derivatives of the aldehydo-acids we observed a body, in the reaction product resulting from nitrous acid and glycocoll ester, in which the group —N=N— had joined itself to carbon. This substance has been termed diazo-acetic ester, produced according to the equation:

$$CO_2C_2H_5.CH_2NH_2+NOOH=CO_2C_2H_5.CH(N_2)+2H_2O.$$

The moderated action of nitrous acid upon the salts of aromatic primary amines is analogous to its action upon aliphatic a-amido-acid esters. It was, however, observed long before the latter. When nitrous acid acts upon the aqueous solution of salts of primary aromatic amines without cooling the mixture, there follows, as in the case of the aliphatic amines, a replacement of the amido-group by hydroxyl:

$$C_6H_5NH_2HCl+NOOH=C_6H_5OH+N_2+H_2O+HCl.$$

Upon cooling the solution, however, the three hydrogen atoms will be replaced by a nitrogen atom, thus:

$C_6H_5NH_2Cl + NOOH = C_6H_5NCl{\equiv}N + 2H_2O$
Diazo-benzol chloride

$C_6H_5NH_2ONO_2 + NOOH = C_6H_5N(O.NO_2){\equiv}N + 2H_2O$
Diazo-benzol nitrate

$C_6H_5NH_2OSO_3H + NOOH = C_6H_5N(O.SO_3H){\equiv}N + 2H_2O$
Diazo-benzol sulphate.

These aromatic diazo-bodies differ from the aliphatic, in that the bivalent group N_2 is linked, not with both, but only with one, affinity to the carbon atom. The second affinity is joined to another univalent radicle. Bodies of this class, when boiled with water, yield oxy-compounds:

$$CO_2C_2H_5.CHN_2+H_2O=CO_2C_2H_5.CH_2OH+N_2$$
$$C_6H_5N_2Cl+H_2O=C_6H_5OH+HCl+N_2.$$

Formation of Diazo-benzols.—(1*a*) Gaseous nitrous acid, made by digesting arsenious acid with nitric acid, is conducted into a paste of the salt to be diazotised. The mixture is cooled all the while with ice. The solution of the diazo-compound is precipitated by a mixture of alcohol and ether. (1*b*) Add acid to the cooled solution of the salt to be diazotised sufficient (B. **8,** 1073; **25,** 1974, footnote; **29,** R. 1158) to liberate the nitrous acid from sodium or potassium nitrite, the well-cooled solution of which is gradually introduced into the acidified liquid:

$$C_6H_5NH_2.HCl+HCl+NO_2K=C_6H_5N_2Cl+2H_2O+KCl.$$

(1*c*) Feebly basic amines, *e.g.* dinitraniline, which are incapable of forming stable salts in aqueous solution, are dissolved in concentrated nitric acid, and the amount of potassium metabisulphite required for reducing 1 mol. nitric acid to nitrous acid is introduced (B. **42,** 2956):

$$2C_6H_5NH_2.HNO_3+K_2S_2O_5+2NO_2H=2C_6H_5N_2NO_3+K_2S_2O_7+4H_2O.$$

(2) As the diazo-benzol salts are more freely soluble in water than in alcohol, in order to obtain solid diazo-salts the diazotising, where practicable, should be made with alkyl nitrites (Vol. I.) dissolved in alcohol or glacial acetic acid (cp. B. **34,** 3338; C. 1898, I. 295; II. 742).

Sometimes a peculiar migration of the diazo-groups takes place, on mixing the solution of an aniline salt with a diazo-salt solution. Thus, toluol diazo-chlorides and nitranilines (B. **29,** 287) arise from nitro-diazo-benzol chlorides and toluidins:

$$NO_2C_6H_4N_2Cl+C_6H_4(CH_3)NH_2=NO_2C_6H_4NH_2+C_6H_4(CH_3)N_2Cl.$$

(3) Another procedure, occasionally applicable in diazotising, consists in letting zinc dust and hydrochloric acid act upon the nitrate of the diazo-derivative (B. **16,** 3080):

$$C_6H_5NH_2.NO_3H+Zn+3HCl=C_6H_5N_2Cl+ZnCl_2+3H_2O.$$

(4) By the action of hydroxylamine upon the nitroso-benzols:

$$C_6H_5NO+H_2NOH=C_6H_5N_2OH+H_2O.$$

(5) Diazo-benzol nitrate is precipitated upon conducting nitric oxide into a chloroform solution of nitroso-benzol (B. **30,** 512).

(6) By the saponification of nitroso-acetanilide with caustic alkali.

(7) By the action of mercuric oxide upon the phenyl-hydrazins.

(8) From phenyl-hydroxylamine, benzol-sulphydroxamic acid, and caustic soda (B. **37,** 290):

$$C_6H_5NHOH+C_6H_5SO_2.NHOH+NaOH=C_6H_5N_2OH+C_6H_5SO_2Na+2H_2O.$$

(9) From phenyl-hydrazin salts with H_2O, or by the action of chlorine and bromine upon the alcoholic solution of free phenyl-hydrazins at low temperatures. This last method is very suitable for preparing solid diazonium salts.

(10) From thionyl-phenyl-hydrazone with thionyl chloride, acetyl chloride, and other acid chlorides (A. **270,** 116):

$$C_6H_5NH.N:SO+CH_3COCl=C_6H_5N_2Cl+S+CH_3CO_2H.$$

Properties.—The acid salts of the diazo-compounds are mostly crystalline, colourless bodies, which speedily brown on exposure to the air. They are readily soluble in water, slightly in alcohol, and are precipitated from the latter solution by ether. Consult B. **28,** 1734, 2020, for their electric conductivity and cryoscopic behaviour. They are generally very unstable (B. **24,** 324), and decompose with a violent explosion when they are heated, or struck by a blow.

The diazo-derivatives are very reactive, and enter numerous, readily occurring reactions, in which nitrogen is liberated, and the diazo-group in the benzene nucleus directly replaced by halogens, hydrogen, hydroxyl, and other groups.

History and Constitution.—The diazo-compounds were discovered at the close of the '50's by Peter Griess (A. **137,** 39), who regarded their salts as additions of $C_6H_4N_2$ and acids, *e.g.* HCl. Kekulé demonstrated that the azo-group only replaced one hydrogen of benzene, and held on the opposite side the radicle of the acid, *e.g.* C_6H_5—N =N.Cl (*Z. f. Ch.* N.F. (1866) **2,** 308; *Chemie der Benzolderivate,* **1,** 223). Blomstrand, A. Strecker, and E. Erlenmeyer, sen., however, viewed the diazo-salts as ammonium salts, *e.g.* $C_6H_5N(Cl) \equiv N$.

The proof of the fact that the azo-group N_2 replaces one benzene hydrogen atom is supposed to be found in the existence of such bodies as tetrabromo-benzol-sulphanile-diazide $C_6Br_4\langle^{N_2}_{SO_3}\rangle$ (B. **10,** 1537). The relations of the *diazo-benzol salts* to the *hydrazins* (E. Fischer, A. **190,** 100), and to the *mixed azo-compounds,* argued in favour of Kekulé's hypothesis.

In recent years Blomstrand's formula has been accepted for the acid salts of the diazo-bodies (B. **29,** R. 93, 783). Comparative studies of the cryoscopic behaviour, and the electric conductivity, of diazo-salt solutions on the one side, and ammonium and alkali salts on the other (B. **28,** 1734, 2020), have contributed to this assumption. The diazo-salts are compared to the quaternary ammonium salts:

$$C_6H_5N\overset{Cl}{\vdots}N \qquad\qquad C_6H_5N\overset{Cl}{\vdots}(CH_3)_3$$

and therefore are termed *diazonium salts.* From a chemical standpoint this view would indicate, among other things, the power of the diazonium haloids to form additive compounds with the halogens—a property which they would hold in common with quaternary ammonium halides as well as with certain alkali metals—*e.g.* cæsium, rubidium. This formula also permits of the easy conversion of the aniline salts by means of nitrous acid into diazo-salts, without being compelled to assume, as is necessary in the Kekulé formula, the migration of the acid residue from the aniline nitrogen to the nitrogen atom, which has but recently entered:

$$C_6H_5\overset{Cl}{NH_3}+NO_2H=C_6H_5\overset{Cl}{N\equiv N}+2H_2O.$$

The basic hydrates corresponding to the diazonium salts are very unstable (cp. B. **31,** 340, 1612; **33,** 2147), as they probably transform themselves into compounds of Kekulé's diazo-type (see above) with atomic displacement. The chemical character of these transposed

hydrates (incapable of isolation) is thereupon changed: they are acids, forming metallic salts such as $C_6H_5N:NOK$, which can be handled. By mineral acids, these metallic salts are changed back into the diazonium salts of the acids. The *diazo-alkali salts*, or *alkaline diazotates*, are transposed into the more stable iso-diazotates, partly at ordinary temperatures, partly on heating (B. **29**, 455). These are distinguished by the difficulty with which they "couple" in alkaline solution, when efforts are made to form azo-dyes, with aromatic amines or phenols (Schraube and Schmidt, B. **27**, 514). To these iso-diazotates the structure $C_6H_5NMe.NO$ was originally ascribed. They were derived from the "nitrosamine" form of the diazo-bodies, since, with methyl iodide, they yielded phenyl-methyl-nitrosamine. But it has been found possible, in several cases, to obtain, from the iso-diazotates, acid hydrates containing hydroxyl, by acidulating them. But these, as a rule, change rapidly into the more stable "nitrosamine" forms ArNH.NO (cp. Vol. I., Pseudo-acids, and B. **35**, 2964).

According to Hantzsch (*Die Diazoverbindungen*, Stuttgart, 1902), the isomerism of the diazo-metallic salts of identical structure is based upon stereo-isomerism (see Vol. I., Stereo-isomerism of ethylene derivatives, and Vol. II., Benzaldoxime), according to the formula:

C_6H_5N	C_6H_5N
$KO\dot{N}$	$\dot{N}OK$
Syn-diazo-benzol-potassium	**Anti-diazo-benzol-potassium.**

The difference in the coupling power (see above), and in other reactions of the normal and the iso-diazotates, respectively, is attributed by Hantzsch to the larger energy content of the former, in comparison with the latter; the two groups of diazotates might therefore also be distinguished as the "unstable" and "stable" groups respectively (see also Vol. I., Dynamic isomerism).

There are therefore four classes of diazo-bodies, also more or less convertible into one another: (1) diazonium salts; (2) normal, "syn-," or "unstable" diazotates; (3) iso-, "anti-," or "stable" diazotates; (4) primary nitrosamines. Their transitions correspond to the following scheme:

$$C_6H_5N(OH)N \rightleftarrows C_6H_5N:N(OH) \rightleftarrows C_6H_5NH.NO.$$

As of the diazo-metallic salts, so also of the diazo-benzol-sulphonic salts, and especially of the diazo-cyanides (see below), isomeric series have been discovered: ArN_2CN may be diazonium cyanide as well as unstable, or stable, diazo-cyanide (benzol-azo-cyanide, cp. nomenclature, B. **33**, 2556).

1. DIAZONIUM SALTS.—**Diazo-benzol chloride** $C_6H_5NCl\equiv N$, colourless needles (B. **23**, 2996; **28**, 2053). The platinum salt, $[C_6H_5N_2Cl]_2PtCl_4$, consists of yellow prisims. The gold salt, $C_6H_5N_2Cl.AuCl_3$ (A. **137**, 52). Mercury salt, $C_6H_5N_2Cl.HgCl_2$, consists of white needles, decomposing at 122°.

Diazo-benzol bromide $C_6H_5.N_2Br$ separates in white laminæ, if bromine be added to the ethereal solution of diazo-amido-benzol. Tribrom-aniline remains in solution.

Diazo-benzol bromide cuprous bromide $C_6H_5N_2Br.Cu_2Br_2$, con-

sisting of reddish-yellow needles, is decomposed by water into cuprous bromide, nitrogen, and bromo-benzol (B. **28**, 1741). Concerning **Benzol-diazonium fluorides** like $C_6H_5N_2F.HF$, and benzol-diazonium-azides like $NO_2C_6H_4N_2.N_3$, see B. **36**, 2056, 2059.

Diazo-per-halides.—The diazonium halides readily add two halogen atoms, but of the ten possible combinations with the halogens, chlorine, bromine, and iodine, the trichloride is the only one that has not been prepared. It may be remarked that the compound $C_6H_5N_2BrICl$ can be prepared both from the chloride and BrI, and from the bromide and ClI (B. **28**, 2754).

Diazo-benzol perbromide $C_6H_5.N_2Br_8$ is precipitated from the aqueous solution of diazo-benzol nitrate or sulphate by bromine in HBr acid or NaBr. It is a dark-brown oil, which quickly becomes crystalline. It is insoluble in water and ether, and crystallises from cold alcohol in yellow laminæ. Continued washing with ether converts it into diazo-benzol bromide. In moist air it decomposes, forming phenol and tribromo-phenol. Chemically, it behaves like a mixture of diazo-benzol bromide and free bromine. Many compounds may thus be brominated with diazo-benzol perbromide, with simultaneous formation of HB and benzol-diazonium bromide. It is changed by aqueous ammonia to diazo-benzol imide. Alkalies decompose it into nitroso-benzol and potassium-diazo-benzol. Boiling alcohol converts it into bromo-benzol.

Diazo-benzol nitrate $C_6H_5N_2O.NO_3$ consists of long, colourless needles, which explode with greater violence than fulminating mercury or nitrogen iodide when they are gently heated, struck, or subjected to pressure.

Diazo-benzol sulphate $C_6H_5.N_2.SO_4H$ consists of colourless needles or prisms, which dissolve readily in water. It explodes at 100°. It is prepared either by diazotising aniline sulphate or by allowing sulphuric acid to act upon diazo-benzol nitrate (B. **28**, 2049).

Diazo-benzol perchlorate $C_6H_5N_2O.ClO_4$ is distinguished by its difficult solubility, like potassium perchlorate. On adding perchloric acid to an aqueous solution of diazo-benzol chloride, it precipitates in the form of prismatic needles, which explode with extreme violence, even in a moist condition.

Oxalate (B. **28**, 2059).

Carbonate, nitrite, acetate (B. **28**, 1741).

Diazonium cyanides, corresponding to diazonium haloids, have been obtained in the form of their silver double cyanides, *e.g.* **p-bromo-diazonium silver cyanide** $BrC_6H_4N(CN)N.AgCN$ (B. **30**, 2546; cp. also **anisol-diazonium cyanide**, B. **34**, 4166); the diazonium cyanides are equally isomerised to diazo-cyanides.

Diazo-benzol sulphocyanide $C_6H_5N_2.SCN$ is a yellow, very explosive mass, obtained from diazo-benzol chloride and potassium sulphocyanide. **p-Chloro-diazo-benzol sulphocyanide** $Cl[4]C_6H_4N_2.SCN$ rearranges itself with ease into **p-Sulphocyano-diazo-benzol chloride** $CNS[4]C_6H_4N_2Cl$ (B. **29**, 947). Such a change of place between nucleus-substituting atoms, and the acid residue of the diazonium group, has become known in a number of further cases; it only occurs in the o- and p-positions of the nucleus substituent; thus, 2, 4-dibromo-benzol-diazonium chloride yields a chloro-bromo-diazonium bromide;

and 2, 4, 6-tribromo-diazonium chloride, a dibromo-chloro-diazonium bromide (B. **31,** 1253 ; **33,** 505 ; **36,** 2069).

p-Phenylene-bis-diazo-chloride $C_6H_4(N_2Cl)_2$ consists of yellow-coloured, very explosive needles (B. **30,** 92).

2. NORMAL DIAZO-HYDRATES are not known in a free state. In attempting to separate them by acids from their potassium salts, yellow-coloured, exceedingly explosive, and unstable precipitates are obtained, under certain conditions. These appear to be not hydrates, but anhydrides, *e.g.* **diazo-benzol anhydride** $[C_6H_5N_2]_2O$; **p-chloro-diazo-benzol anhydride** $[ClC_6H_4N_2]_2O$. These bodies redissolve in acids to diazonium salts, in alkalies to diazo-metallic salts, in ammonia to bis-diazo-amido-bodies, in anilines to diazo-amido-compounds (B. **29,** 451), in HCN, diazo-cyanides, and with benzol-sulphinic acid, diazo-sulphones (B. **29,** 451 ; **31,** 637).

Normal diazo-benzol potassium $C_6H_5N_2OK$ is produced on introducing a saturated aqueous solution of diazo-benzol chloride into an excess of highly concentrated caustic potash (B. **29,** 461). It forms white, pearly flakes which can be quantitatively reconverted into diazo-benzol chloride. Normal sodium-diazo-benzol is formed in small quantities by the action of sodium amide upon nitro-benzol (B. **37,** 629), or of NH_2OH upon nitro-benzol in alkaline solution (B. **38,** 2056). It yields diazo-esters in the cold, with alcohols (B. **29,** 488) ; see B. **30,** 339, for the reduction of potassium diazo-benzol to phenyl-hydrazin. When alkaline diazo-benzol solutions are oxidised with potassium ferricyanide or potassium permanganate, the principal product is diazo-benzol acid, together with a little nitroso-benzol, nitro-benzol, azo-benzol, and diphenyl. Benzoyl chloride and sodium hydroxide change normal potassium diazo-benzol into nitroso-benzanilide $C_6H_5N(NO).CO.C_6H_5$ (B. **30,** 214). Salts of the heavy metals with diazo-benzol are obtained by the precipitation of solutions of potassium diazo-benzol with metallic salts (B. **23,** 3035 ; **28,** 226).

Diazo-benzol methyl ether $C_6H_5N_2.OCH_3$, isomeric with methyl-phenyl-nitrosamine, is obtained from normal or iso-diazo-benzol silver and methyl iodide, as well as from diazo-benzol potassium and methyl alcohol. It is a yellow, volatile oil, rapidly turning dark in colour, possessing a penetrating, stupefying odour, and decomposing shortly after its liberation. Boiling dilute sulphuric acid decomposes it into nitrogen-methyl alcohol, and phenol (B. **28,** 227, 236). **o- and p-Nitro-diazo-benzol methyl ether** $NO_2.C_6H_4N_2.OCH_3$ (B. **28,** 236).

On saponification with alkali in the cold, the diazo-ethers give normal diazo-alkali salts (B. **36,** 4361).

Di-p-nitro-phenyl-diazo-sulphide $[NO_2[4]C_6H_4N_2]_2S$ is precipitated as an egg-yellow, very explosive mass, on adding hydrogen sulphide to a neutral solution of the diazo-chloride. With benzene it forms nitro-diphenyl, nitrogen, and sulphur ; di-p-nitro-diphenyl disulphide is formed simultaneously. In an acid solution with an excess of hydrogen sulphide there is produced, along with the diazo-sulphide, **p-Nitro-phenyl-diazo-mercaptan hydrosulphide** $NO_2.C_6H_4N_2SH.SH_2$, consisting of red, brilliant, metallic-looking needles, which dissolve with a deep-red colour in the alkalies. They decompose, when fused, with the formation of nitro-phenyl-hydrazin, nitraniline, sulphur,

and dinitro-phenyl disulphide. Non-explosive **Di-p-nitro-phenyl-diazo-disulphide** $[NO_2C_6H_4N_2]_2S_2$ is finally the third product in the action of hydrogen sulphide. It is insoluble in alkali. It consists of sulphur-yellow needles, soluble in acetone (B. **29,** 272). See Thiophenol for diazo-benzol-thio-phenyl ether.

3. ISO-DIAZO-HYDRATES are liberated from their potassium salts by acetic acid. They are very easily decomposed. Those of benzene and toluol are colourless oils. These substances are mostly, however, not the real hydrates, but their pseudo-forms: primary aryl-nitrosamines ArNH.NO. In some cases, as in the dibrom-anisol-diazo-hydrate, the hydroxyl forms have been isolated as unstable precipitates easily passing into nitrosamines. In undissociating solvents they react energetically with NH_3, acetyl chloride, and PCl_5, whereas the nitrosamine forms remain indifferent (B. **35,** 2964).

Potassium iso-diazo-benzol $C_6H_5N_2OK$ is formed on digesting potassium diazo-benzol for a brief period at 130°–135° with concentrated caustic potash; and when fused, caustic potash acts upon phenyl-methyl-nitrosamine, into which it returns upon treatment with methyl iodide (B. **27,** 514, 672, 680). Sodium amalgam reduces it with ease to phenyl-hydrazin (B. **29,** 473; **30,** 339). With benzoyl chloride and sodium hydrate, as well as during oxidation, it behaves like the normal diazotate, but differs from the latter qualitatively by the omission of dye-formation, *e.g.* on mixing with β-naphthol in alkaline solution (B. **27,** 517). Potassium iso-diazo-benzol is also formed direct from aniline and phenyl-hydrazin by the action of alkyl nitrite and alkali alcoholate, liberating nitrous oxide in the latter case (B. **38,** 3511; **41,** 2808); it has also been obtained from oxy-azoxy-benzol $C_6H_5(N_2O)C_6H_4OH$ by oxidising decomposition with MnO_4K (B. **38,** 1957). **Potassium iso-p-diazo-toluol** results when its isomeride is exposed to the air (B. **29,** 1385). **Sodium iso-p-nitro-diazo-benzol** $C_6H_4(NO_2)N_2ONa+2H_2O$ yields nitro-phenyl-methyl-nitrosamine with methyl iodide, whereas the silver salt forms the corresponding diazo-ester (B. **29,** 1384).

4. DIAZO-BENZOL SULPHONIC ACID, *benzene azo-sulphonic acid* $C_6H_5N_2SO_3H$, is very decomposable (B. **30,** 75). Its potassium salt is produced upon introducing diazo-benzol nitrate into a cold, neutral, or feebly alkaline solution of di-potassium sulphite; the liquid solidifies to a yellow, crystalline mass. Under other conditions a more easily decomposable, orange-coloured salt is formed (B. **27,** 1715, 2930). For the sensitivity of the diazo-benzol sulphonates to light, and their application in photography, consult B. **28,** 3131. Mono-potassium sulphite reduces diazo-benzol nitrate to potassium phenyl-hydrazin sulphonate, which mercuric oxide oxidises to potassium diazo-benzol sulphonate (B. **27,** 1245).

p-Nitro-diazo-benzol nitrate and one molecule of K_2SO_3 yield **potassium p-nitro-diazo-benzol sulphonate,** which also appears to exist in two forms. The acid crystallises, with four molecules of water, in ruby-red prisms (B. **30,** 90). On using two molecules of potassium sulphite the product is potassium p-nitro-phenyl-hydrazin disulphonate $C_6H_4(NO_2)N(SO_3K)NH.SO_3K$ (B. **29,** 1829). **p-Chloro-** and **p-bromo-benzol-diazo-sulphonic acid** (B. **30,** 75).

The *diazonium* salts and benzene-sulphinic acid combine to **Benzene-**

diazo-sulphones $C_6H_5N_2SO_2C_6H_5$, which are resolved by hydrochloric acid into diazonium chlorides and sulphinic acids (B. **30,** 312).

With substances containing the grouping $C_6H_5N:NX$, *e.g.* benzol-diazo-cyanides and the azo-compounds, benzol-sulphinic acid forms colourless addition products, mostly stable in water and acids: $C_6H_5N(SO_2C_6H_5)NHX$. These should be regarded as derivatives of hydrazo-benzol, and are split up into their components by alkalies (B. **30,** 2548). The action of SO_2 upon p-nitro-diazo-benzol hydrate produces **p-Nitro-phenyl-diazo-p-nitro-phenyl sulphone** $NO_2C_6H_4N:NSO_2C_6H_4NO_2$ (B. **35,** 661).

5. DIAZO-BENZOL CYANIDE $C_6H_5N_2CN$ appears as an unstable oil, on adding a potassium cyanide solution to the solution of a diazo-benzol salt. If, however, the reverse be done—the diazo-salt be added to the potassium cyanide solution—a prussic acid additive product, $C_6H_5N_2CN.HCN$, will separate as a yellow precipitate, m.p. 70°. **Benzene-diazo-carboxyl-amide,** *phenyl-azo-carbamide* $C_6H_5N:NCONH_2$, results from the oxidation of phenyl-semicarbazide (*J. Ch. Soc.*, 1895, 1, p. 1067; B. **28,** 1925, 2599). It consists of reddish-yellow needles, m.p. 114°. The *anilide* $C_6H_5N_2CONHC_6H_5$, from 1, 4-diphenyl-semicarbazide (B. **29,** 1691), m.p. 122°.

Two isomerides have been obtained from p-chloro- and p-nitro-diazo-benzol cyanide, and in each instance the one body is unstable and the other stable. The unstable, low-melting modifications only form at lower temperatures, decompose easily, especially in contact with copper powder, give up nitrogen with the formation of benzene cyanides, form azo-dyes with aromatic amines or phenols, and change rapidly, particularly in alcoholic solution, or in sunlight, into the stable isomerides (C. **1906,** II. 1054). This transposition is influenced by the nature and position of the nuclear substituents. With a less straightforward course it can also be obtained through the intermediary of benzol-sulphinic addition products (B. **30,** 2553).

Unstable p-chloro- and p-nitro-diazo-benzol cyanide melt at 28° and 29° respectively, the stable forms at 106° and 86° respectively. **2, 4, 6-Tribromo-benzol-diazo-cyanide,** unstable form, m.p. 60°; stable form, m.p. 147°. The stable cyanides approach, in their behaviour, the azo-bodies. With prussic acid they readily combine to form imido-cyanides (see above); with water, diazo-carboxyl amides; with alcohols, amido-ethers, from which, by saponification, the potassium salts of the corresponding diazo-benzol-carboxylic acids are obtained; the acids are very easily decomposed (B. **28,** 670, 2072; **30,** 2529). Tribromo-benzol-azo-carboxylic acid $C_6H_2Br_3.N_2COOH$ is obtained from its amide, the oxidation product of tribromo-phenyl-semicarbazide (B. **28,** 1929).

CHIEF DECOMPOSITIONS OF THE DIAZO-BENZOL SALTS.

The decompositions of diazo-salts in which atoms of metalloids or atomic groups take the place of nitrogen and expel the latter, are of the greatest importance for the relations of many different di- and poly-substitution products of benzene, and its homologues.

1. **Replacement of the Diazo-group by Hydrogen.**—(*a*) On heating diazonium salts with alcohols, two reactions may take place :

$$\text{I. } C_6H_5N_2Cl+C_2H_5OH=C_6H_5OC_2H_5+HCl+N_2$$
$$\text{II. } C_6H_5N_2Cl+C_2H_5OH=C_6H_6+C_2H_4O+HCl+N_2.$$

Reaction I. yields phenol-ether, and reaction II. benzene-hydrocarbons with aldehyde as a by-product (A. **137,** 69 ; **217,** 189 ; B. **9,** 899 ; **17,** 1917 ; **18,** 65). Often these two reactions are simultaneous : solid benzol-diazonium chloride or sulphate, with absolute methyl-alcohol, gives anisol ; with ethyl-alcohol, phenetol and a little benzene ; in the negatively substituted benzols, the replacement of the diazo-group by hydrogen steps into the foreground. Multi-valent alcohols, on the other hand, only appear to form phenol-ether (B. **34,** 3337 ; **35,** 998 ; **36,** 2061). Sunlight favours reaction I. (C. 1905, II. 129).

Heating with phenols also converts diazonium salts partly into phenyl-ether, with evolution of nitrogen ; but oxy-diphenyls are mainly generated (C. 1903, I. 705).

(*b*) The aryl-hydrazins formed by reduction of the diazo-compounds (cp. phenyl-hydrazin) are so oxidised by boiling with copper sulphate, ferric chloride, potassium chromate, or sodium hypochlorite that an H atom takes the place of the hydrazin group, with evolution of nitrogen :

$$C_6H_5NHNH_2+O=C_6H_6+N_2+H_2O.$$

The intermediate formation of hydrazins, subsequently oxidised by unchanged diazo-compounds (B. **36,** 813), is probably also the cause of the following reactions in which H displaces the diazo-group :

(*c*) Boiling of diazonium chlorides with stannous chloride solution (B. **22,** R. 741).

(*d*) Action of hypo-phosphonic acid upon diazonium salts (B. **35,** 162 ; A. **320,** 143).

(*e*) Solution of the diazo-compound in caustic soda, and soda-stannous oxide (B. **36,** 813). Iso-diazotates are not reduced by the latter (B. **36,** 2065).

(*f*) Boiling with formic acid converts diazonium salts, almost exclusively, into the corresponding hydrocarbons :

$$C_6H_5N_2Cl+HCOOH=C_6H_6+N_2+CO_2+HCl.$$

Glacial acetic acid yields nothing but acetyl-phenols (B. **28,** 1632 ; C. 1907, I. 1031).

2. **Replacement of the Diazo-group by Halogens.**—(*a*) The diazo-benzol salts are treated with haloid acids. Of the four acids of this class, hydriodic acid reacts most readily :

$$C_6H_5N_2.OSO_3H+HI=C_6H_5I+N_2+SO_4H_2.$$

The haloid acids are frequently applied in glacial acetic acid solution. The hydro-bromides or hydro-iodides of the bases can also be treated with nitric acid.

(*b*) Concentrated haloid acids are allowed to act upon the diazo-amido-derivatives. This reaction is especially recommended for the preparation of fluoro- or chloro-derivatives (B. **21,** R. 97) :

$$C_6H_5.N:N-NH.C_6H_5+2HFl=C_6H_5Fl+N_2+FlH.NH_2.C_6H_5.$$

(*c*) Chloro- and bromo-derivatives are formed, if the $PtCl_4$- and $PtBr_4$- double salts are heated alone; or, which is better, with dry soda or salt:

$$(C_6H_5N_2Cl)_2PtCl_4 = 2C_6H_5Cl + 2N_2 + Pt + 2Cl_2.$$

(*d*) When the diazo-perbromides are boiled with alcohol (the latter is oxidised to aldehyde), bromo-benzols are formed:

$$C_6H_5N_2Br_3 + CH_3CH_2OH = C_6H_5Br + N_2 + 2HBr + CH_3CHO.$$

The reactions indicated under *a*, *b*, *c*, and *d* were all observed by P. Griess. Another reaction belongs to this group; it was discovered by Sandmeyer (B. **17,** 2650; **23,** 1880), and is capable of far greater generalisation. It is based upon the fact that diazo-salts are decomposed by cuprous salts:

(*e*) When cuprous chloride is added to an aqueous solution of diazo-benzol chloride, an addition product, $C_6H_5N_2ClCu_2Cl_2$, is formed at first, but upon the application of heat this decomposes into C_6H_5Cl (B. **19,** 810; **23,** 1628; **33,** 2544):

$$C_6H_5N_2Cl(Cu_2Cl_2) = C_6H_5Cl + N_2 + Cu_2Cl_2.$$

Cuprous bromide and cuprous iodide act similarly upon the corresponding diazo-benzol salts. If cuprous bromide acts upon a diazonium salt, the corresponding bromo-benzol is produced under suitable conditions, which proves that the cuprous haloid takes an essential part in the process.

A modification of the method consists in treating the diazo-derivatives in the presence of hydrochloric, hydrobromic, or hydro-iodic acid with copper powder (B. **23,** 1218; **25,** 1091, footnote). The latter seems to act catalytically.

3. **Replacement of the Diazo-group by Hydroxyl.**—When the salts (sulphates are best) are boiled with water, the diazo-group will be replaced by hydroxyl:

$$\begin{aligned} C_6H_5N_2Br \quad + H_2O &= C_6H_5OH + N_2 + HBr \\ C_6H_5N_2NO_3 + H_2O &= C_6H_5OH + N_2 + NO_3H \\ C_6H_5N_2SO_4H + H_2O &= C_6H_5OH + N_2 + SO_4H_2. \end{aligned}$$

This method often fails in negatively substituted diazonium salts. But it also succeeds, in these cases, on replacing the water by a mixture of dilute sulphuric acid and sodium sulphate (C. 1905, II. 617).

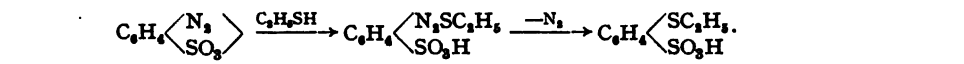
On decomposing diazo-nitrates, nitro-phenols are formed as by-products. On the velocity of phenol splitting, see A. **825,** 292; B. **31,** 3519.

4. **Replacement of the Diazo-group by the Sulphydrate Group.**—On digesting the diazide of sulphanilic acid (*q.v.*), a cyclic diazo-salt, with alcoholic potassium sulphide, the potassium salt of p-thio-phenol-sulphonic acid will be produced (B. **20,** 350):

$$C_6H_4\begin{cases}[1]N_2 \\ [4]SO_3\end{cases} + K_2S = C_6H_4\begin{cases}[1]SK \\ [4]SO_3K\end{cases} + N_2.$$

In the same manner, when mercaptan acts upon diazo-benzol-

sulphonic acid, a compound results which, upon standing or warming, decomposes into thio-phenol-ethyl-ether-p-sulphonic acid:



With xanthogenic salts (Vol. I.) the diazonium salts form aromatic xanthogenic acid esters, like $C_6H_5S.CSOC_2H_5$, which, on saponification, yield thio-phenols (*J. pr. Ch.* 2, **41**, 184).

For the reaction of diazonium salts with thio-glycolic acid, see C. 1908, I. 1221.

5. **Replacement of the Diazo-group by the Sulphinic Acid Residue** is brought about by conducting sulphurous acid through solutions of diazonium sulphates, or treating them with alcoholic SO_2 solution, bisulphite, and Cu powder (B. **32**, 1136; C. 1902, I. 959):

$$C_6H_5N_2(SO_4H)+SO_2+Cu=C_6H_5SO_2H+N_2+SO_4Cu.$$

6. **Replacement of the Diazo-group by the Nitro-group.**—The diazo-benzol nitrite solution is added to freshly precipitated cuprous oxide, or the solutions of diazonium, and mercury nitrites, are decomposed with Cu powder (B. **33**, 2551).

7. In a few cases the diazo-group may be replaced by amine residues, *e.g.* in the diazide of amido-anthra-quinone-sulphonic acid by treatment with ammonium carbonate or amines (B. **35**, 2593).

8. **Replacement of the Diazo-group by the Cyanogen Group.**—This reaction connects by easy stages the nitro-amido-benzols with the nitro-benzoic acids, and the latter with the phthalic acids. The importance of this fact has been mentioned. Add the diazo-benzol chloride solution to a copper sulphate solution mixed with potassium cyanide (B. **20**, 1495; **23**, 1630):

$$C_6H_5N_2CN=C_6H_5CN+N_2.$$

9. Sulpho-cyanides (rhodanides) result when the diazo-salts are boiled with potassium, and cuprous sulpho-cyanides (B. **23**, 770).

10. When a solution of diazo-benzol sulphate is mixed with potassium cyanate, and reduced copper is then added (B. **25**, 1086), phenyl iso-cyanide or carbanile will result.

11. **Formation of Diphenyl Compounds from Diazo-derivatives.**—Diphenyl derivatives frequently appear as by-products in the treatment of diazo-bodies with reducing agents—*e.g.* stannous chloride (B. **18**, 965), alcohol, and reduced copper (B. **23**, 1226), alcohol alone or sodium ethylate (B. **28**, R. 389)—as well as in the action of water, of phenol (B. **23**, 3705), and of potassium ferricyanide (B. **26**, 471). Into aromatic hydrocarbons and heterocyclic compounds—*e.g.* thiophene, pyridin, and quinolin—diazo-benzol chloride introduces the phenyl group. This occurs very easily in the presence of aluminium chloride (B. **26**, 1994):

$$C_6H_5N_2Cl + C_6H_6 \xrightarrow{Al_2Cl_6} C_6H_5C_6H_5 + N_2 + HCl.$$

The diazo-residue in the diazo-oxides, diazo-sulphides, and iso-

diazo-hydrates is readily replaced by cyclic residues (B. **28,** 404 ; **29,** 165, 274, 452) :

$$[NO_2C_6H_4N_2]_2S+2C_6H_6=2NO_2C_6H_4.C_6H_5+N_2+H_2S$$
$$C_6H_5N_2OH+C_5H_5N \text{ (pyridin)}=C_6H_5.C_5H_4N+N_2+H_2O.$$

12. On treating diazonium salts with amm. cuprous oxide solution, they are mostly converted into azo-benzols with evolution of N :

$$2C_6H_5N_2Cl+Cu_2O=C_6H_5N : NC_6H_5+N_2+CuCl_2+CuO ;$$

whereas the diazonium salts, from o- and p-nitraniline, usually give the corresponding diphenyl derivatives (A. **320,** 122).

13. The reactions 11 and 12 are simultaneous when saturated potassium ferrocyanide solution acts upon diazonium salts, the azo-compounds of the diphenyl series being produced (C. 1907, I. 1789).

Other Reactions of Diazo-derivatives, in which nitrogen is not set free :

1. Phenyl-hydrazins are produced in the reduction of diazo-salts.

The action of benzol-diazonium chloride upon zinc-ethyl, in etheric solution, produces ethylated phenyl-hydrazins and also diethyl-benzidin (B. **35,** 4179 ; C. 1905, I. 79).

2. When diazo-compounds are oxidised in alkaline solution, they are converted into nitroso-benzol and phenyl-nitro-amine or diazo-benzol acid.

3. The behaviour of diazo-bodies toward ammonia, alkylamines, aniline, and related bases, when diazo-imido-, diazo-amido-, and mixed azo-derivatives arise, is worthy of special note. These very important reactions will be given in detail, with the individual classes.

4. Hydrazones result when diazo-benzol, in alkaline solution, acts upon bodies containing the group CH_2CO. The primarily formed hydrazones often rearrange themselves, with additional quantities of the diazo-benzol salt, into formazyl derivatives, which belong to the class of amidines (B. **27,** 147, 320, 1679 ; **29,** 1386 ; **31,** 3122 ; **32,** 2880).

9. Diazo-amido-compounds.

10. Dis-diazo-amido-compounds.

The diazo-amido-compounds are derived from the unknown hydride $NH=N—NH_2$, in which the hydrogen of the imide group is replaced by an aromatic residue—*e.g.* phenyl, tolyl, etc.—and the hydrogen of the amido-group by aliphatic or aromatic residues : mixed and true aromatic diazo-amido-compounds. The dis-diazo-amido-bodies are also derivatives of an unknown nitrogen hydride, $NH=N—NH—N=NH$.

Formation of Diazo-amido-derivatives.—They result from the transposition of primary and secondary amines with diazo-salts :

1*a*. Primary aromatic amines yield diazo-amido- or dis-diazo-amido-bodies, depending upon the conditions of experiment. Diazo-amido-compounds are formed when equimolecular quantities of diazo-salt and primary amine interact :

$$C_6H_5N_2.Cl+NH_2C_6H_5=C_6H_5N : N.NHC_6H_5+HCl.$$

Substituted anilines containing the substituent in p- or o-position react essentially like aniline itself, but in meta-substituted anilines, like m-toluidin, the formation of amido-azo-compounds becomes prominent (*J. pr. Ch.* 2, **65**, 401).

Diazo-amido-compounds are also produced when an alkali nitrite, in the absence of mineral acids, acts upon the salts of primary amines :

$$2C_6H_5NH_2HCl+NO_2K=C_6H_5N:N.NH.C_6H_5+KCl+HCl+2H_2O.$$

1*b*. A dis-diazo-compound results if a molecule of aniline be allowed to act, in alkaline, alcoholic solution, upon two molecules of a diazo-benzol salt. It can also be obtained by transposing diazo-benzol chloride with diazo-amido-benzol (B. **27**, 703) :

$$2C_6H_5N_2Cl+C_6H_5NH_2=\begin{matrix}C_6H_5N:N\\C_6H_5N:N\end{matrix}\!\!>\!NC_6H_5+2HCl$$

$$C_6H_5N_2Cl+C_6H_5N:N.NHC_6H_5=\begin{matrix}C_6H_5N:N\\C_6H_5N:N\end{matrix}\!\!>\!NC_6H_5+HCl.$$

Primary aliphatic amides react, with special readiness, with diazo-benzol chloride, forming dis-diazo-amido-compounds, so that the isolation of the simple aliphatic-aromatic diazo-amido-compounds only succeeds under special conditions (B. **38**, 2328).

When a diazo-benzol salt solution is allowed to flow into cold, concentrated ammonia, dis-diazo-benzol-amide $C_6H_5N:N.NH.N:NC_6H_5$ (B. **28**, 171) will be produced.

The normal diazo-alkali salts also yield diazo-amido-compounds (B. **29**, 289). The iso-diazo-salts, due to the transposition, are, however, generally incapable of reactions.

1*c*. Secondary aromatic and aliphatic bases yield secondary aromatic, or mixed aliphatic-aromatic, diazo-amido-compounds (B. **8**, 148, 843 ; C. 1905, I. 1539).

2. Diazo-amido-compounds are also produced by the action of free nitrous acid upon alcoholic solutions of free primary amines, the free diazo-benzol hydrate or anhydride first formed turning into aniline :

$$C_6H_5N_2.OH+NH_2C_6H_5=C_6H_5N:N.NHC_6H_5+H_2O.$$

If nitrites, such as silver nitrite, act upon free aniline, salts of the diazo-amido-compounds are generated (B. **29**, R. 1158).

3. A method specially useful for preparing mixed fatty-aromatic diazo-amido-compounds is based upon the action of organo-magnesium compounds upon the aryl esters of nitrogen hydride. Addition products containing Mg are first formed, and from these water liberates the diazo-amido-compounds (D. **38**, 683) :

$$C_6H_5.N\!<\!\begin{matrix}N\\\|\\N\end{matrix}\!\!+CH_3.Mg.I=C_6H_5.N:N.N(MgI)CH_3$$

$$C_6H_5N:N.N(MgI)CH_3+H_2O=C_6H_5N:N.NHCH_3+MgI(OH).$$

4. Nitrosamines, and primary amines, also yield diazo-amido-compounds (B. **27**, 655).

Nitroso-acetanilide undergoes transposition with aniline, acetic acid and diazo-amido-benzol being formed. If 1 mol. aniline is used

for every 2 mols. nitroso-acetanilide in an alkaline solution, an aromatic dis-diazo-amido-compound is obtained :

$$\begin{matrix} C_6H_5 \\ CH_3CO \end{matrix}\!\!>\!N\!-\!NO + NH_2C_6H_5 = C_6H_5NH\!-\!N\!=\!NC_6H_5 + CH_3COOH$$

$$2\,\begin{matrix} C_6H_5 \\ CH_3CO \end{matrix}\!\!>\!N\!-\!NO + NH_2C_6H_5 = \begin{matrix} C_6H_5N\!=\!N \\ C_6H_5N\!=\!N \end{matrix}\!\!>\!NC_6H_5 + 2CH_3COOH.$$

Course of the Reaction in the Formation of Diazo-amido-derivatives.—It is an interesting fact that the same diazo-benzol-p-amido-toluol is formed, *e.g.*, from diazo-benzol chloride and p-toluidin, as from diazo-p-toluol chloride and aniline, although different compounds might well have been expected :

$$C_6H_5N_2Cl + NH_2[4]C_6H_4[1]CH_3 \longrightarrow \text{I. } C_6H_5N\!=\!N.NH[4]C_6H_4[1]CH_3$$
$$CH_3[1]C_6H_4[4]N_2Cl + NH_2C_6H_5 \longrightarrow \text{II. } CH_3[1]C_6H_4[4]N\!=\!N.NHC_6H_5.$$

By method 3, the transposition of phenyl-azide with p-tolyl-magnesium bromide, and of p-tolyl-azide with phenyl-magnesium bromide, identical products are also obtained.

The constitution of the substances produced is best determined by transposing them into phenyl iso-cyanate. Thus, diazo-benzol-p-amido-toluol forms a urea with this reagent, and this new compound will have either formula I'., corresponding to I., or II'., corresponding to formula II., depending upon the constitution of the diazo-amido-body :

$$\text{I'. } CO\!<\!\begin{matrix} NHC_6H_5 \\ N\!<\!\begin{matrix} [4]C_6H_4[1]CH_3 \\ -N\!=\!N.C_6H_5 \end{matrix} \end{matrix} \longrightarrow CO\!<\!\begin{matrix} NHC_6H_5 \\ NH[4]C_6H_4[1]CH_3 \end{matrix} + C_6H_5OH + N_2$$

$$\text{II'. } CO\!<\!\begin{matrix} NHC_6H_5 \\ N\!<\!\begin{matrix} C_6H_5 \\ N\!=\!N[4]C_6H_4[1]CH_3 \end{matrix} \end{matrix} \longrightarrow CO\!<\!\begin{matrix} NHC_6H_5 \\ NHC_6H_5 \end{matrix} + CH_3[1]C_6H_4[4]OH + N_2.$$

On decomposing the urea with dilute sulphuric acid, the products will be phenyl-p-tolyl-urea, phenol, and nitrogen ; whereas, according to formula II'., they should be sym. diphenyl-urea, p-cresol, and nitrogen. Therefore, diazo-benzol-amido-p-toluol is constituted according to formula I. The imide group apparently combines with the more negative radicle (B. **21**, 2578 ; **40**, 2395).

Diazo-amido-compounds from Primary Aromatic Bases.

Diazo-benzol-amide, *phenyl-triazene* $C_6H_5N : N.NH_2$, m.p. 50° with decomposition. Diazo-benzol-amide is the simplest conceivable diazo-amido-compound. Its formation, by the action of ammonia upon benzol-diazonium chloride, is not practicable, only dis-diazo-benzol-amide being formed. It is obtained by reduction of diazo-benzol-imide with stannous chloride and HCl in ether at −18° :

$$C_6H_5N\!<\!\begin{matrix} N \\ \| \\ N \end{matrix} + 2H = C_6H_5N : N.NH_2.$$

The cupro-salt forms yellow prismatic crystals. Diazo-benzol-amide is exceedingly unstable. It decomposes spontaneously in a short time, but instantly, in contact with acids, in aniline, and nitrogen.

It combines with phenyl iso-cyanate to form benzol-azo-phenyl-urea $C_6H_5N : N.NHCO.NHC_6H_5$. Oxidisers like potassium hypobromite, or ammoniacal silver solution, turn it into diazo-benzol-imide (B. **40,** 2376).

Diazo-amido-benzol, *benzol-diazo-anilide, diazo-benzol-anilide* (B. **14,** 2443, footnote) $C_6H_5.N_2.NH.C_6H_5$, melts at 96°, and explodes when it is heated to higher temperatures. It is obtained by the action of nitrous acid on the cold alcoholic solution of aniline (Griess, A. **121,** 258); by mixing diazo-benzol nitrate with aniline (B. **7,** 1619); and by pouring a slightly alkaline sodium nitrate solution upon aniline hydro-chloride (B. **8,** 1074) or sulphate with cold sodium nitrite (B. **17,** 641; **19,** 1953; **20,** 1581).

The combination of diazo-benzol-imide with phenyl-magnesium bromide gives a salt of diazo-amido-benzol, of the formula $C_6H_5N_2N(MgBr)C_6H_5$, where it can be liberated by water (B. **36,** 910).

Diazo-amido-benzol consists of golden-yellow, shining laminæ or prisms. It is insoluble in water, sparingly soluble in cold, but readily in hot alcohol, ether and benzene. Its transpositions will be discussed later; the most remarkable one is its rearrangement into isomeric *amido-azo-benzol.*

Its salts are very unstable, although it forms a double salt, $(C_{12}H_{11}N_3.HCl)_2.PtCl_4$, with hydrochloric acid and $PtCl_4$. It crystallises in reddish needles. When the alcoholic solution is mixed with silver nitrate, the compound $C_6H_5.N_2NAg.C_6H_5$ separates in reddish needles.

Sodium, in ethereal solution, converts it into $C_6H_5NNaN=N.C_6H_5$, which is decomposed by water (B. **27,** 2315). Cuprous salt, C. 1900, I. 659.

Benzene-diazo-acetanilide $C_6H_5N=N—N(COCH_3)C_6H_5$ melts with decomposition at 130°, and is formed when diazo-amido-benzene stands with acetic anhydride in toluene solution (B. **24,** 4156).

The *para*-variety of the three diazo-amido-toluenes is alone stable. The *ortho-* and *meta*-forms (from ortho- and meta-toluidine) immediately pass into isomeric amido-azo-derivatives.

Diazo-amido-compounds containing two different residues: Mixed diazo-amido-compounds, like **Diazo-benzol-p-amido-bromo-benzol,** melting at 91° (B. **20,** 3012).

o-, m-, p-Dinitro-diazo-amido-benzol, m.p. 196°, 194°, 228° (B. **27,** 2201; **28,** R. 303), diazo-benzol-p-amido-toluol, can be obtained from the diazo-derivatives of the two components with the free amido-derivatives—*e.g.* **Diazo-benzol-p-amido-toluol** equally well from the diazo-benzol salt with p-toluidin, as from p-diazo-toluol salt and aniline.

Dis-diazo-benzol-amide $(C_6H_5N : N)_2NH$ (B. **27,** 899) is extremely decomposable. **Dis-diazo-benzol-anilide** $C_6H_5N=N—N(C_6H_5)—N=NC_6H_5$ consists of shining yellow flakes which explode at 80°–81° in a capillary tube (B. **27,** 703, 2597; C. 1905, I. 517).

Mixed Fatty-aromatic Diazo-amido-compounds.

Diazo-benzol-methyl-amide, *methyl-phenyl-triazene* $C_6H_5N : N.NHCH_3$, colourless plates, m.p. 37°, obtained from diazo-benzol-

imide and methyl-magnesium iodide. With water vapour it volatilises without decomposition. With acids it is decomposed into aniline, nitrogen, and the ester of methyl-alcohol. With phenyl isocyanate it forms a **urea** of m.p. 104°, which is split, by HCl, into benzol-diazonium chloride, and methyl-phenyl-urea.

Copper-methyl-phenyl-triazene $C_6H_5N_3CuCH_3$, orange-yellow prisms, m.p. 187° with decomposition.

Acetyl-methyl-phenyl-triazene $C_6H_5N : N.N(COCH_3)CH_3$, m.p. 35° (B. **38,** 678). **Diazo-benzol-ethyl-amide,** colourless crystals, m.p. 31°. **p-Tolyl-methyl-triazene** $CH_3C_6H_4N : N.NHCH_3$, m.p. 81·5° (B. **40,** 2397). **Diazo-benzol-dimethyl-amine** $C_6H_5N=N.N(CH_3)_2$, a yellowish oil (B. **8,** 148). **Diazo-benzol-piperidin** $C_6H_5N=N.NC_5H_{10}$, m.p. 43°. The diazo-piperidins are useful for preparing fluorine compounds.

Benzol-azo-cyanamide, *phenyl-cyano-triazene* $C_6H_5N : N.NHCN$ or $C_6H_5NH.N : N.CN$, colourless flakes puffing off at 72°. The potassium salt is formed by heating diazo-benzol-imide with KCN in alcohol. Acids split it up into diazo-benzol and urea :

$$C_6H_5N : N.NHCN + 2H_2O = C_6H_5N_2OH + CO(NH_2)_2.$$

Methylation of the potassium salt yields **methyl-phenyl-cyano-triazene** $C_6H_5(CH_3)N.N : NCN$, m.p. 69°–70°, decomposed by acids into methyl-aniline, nitrogen, and cyanic acid (B. **37,** 2374).

Dis-diazo-benzol-methyl-amine $(C_6H_5N=N)_2NCH_3$, light-yellow needles, m.p. 112°. **Dis-diazo-benzol-ethyl-amine,** m.p. 70° (B. **22,** 934).

The Rearrangements of the Diazo-amido-compounds.

1. The most remarkable property of the diazo-amido-compounds, containing a replaceable hydrogen atom in the p-position with reference to the NH group, is their ability to rearrange themselves into isomeric p-amido-azo-derivatives. In the amido-azo-body the amido-group holds the p-position with reference to the point of union :

$$C_6H_5N=N—NHC_6H_5 \longrightarrow C_6H_5N=N[1]C_6H_4[4]NH_2.$$

This rearrangement completes itself in the course of a few days, when a small quantity of an aniline salt is present. It may be assumed that in the conversion a quantity of aniline, equal to that actually needed for the change, is produced ; consequently a comparatively small amount of the aniline salt will be sufficient to rearrange a large quantity of diazo-amido-benzol into amido-azo-benzol (Kekulé, *Z. f. Ch.* (1866), 689 ; B. **25,** 1376). The rapidity of the conversion is proportional to the strength of the acid whose aniline salt is employed (B. **29,** 1899). A strong base, such as amido-azo-benzol, is obtained from a body indifferent to acids—*e.g.* diazo-amido-benzol. Various intramolecular atomic rearrangements, such as the preceding, in which indifferent compounds are rearranged as strong bases or strong acids, are known—*e.g.* the rearrangement of hydrazo-benzol as benzidin, of benzol into benzilic acid, etc. (I. 54 ; II. 116, 118).

2. The imide hydrogen of the diazo-amido-benzol can be replaced by acid radicles, through the action of acid anhydrides (see Benzene-diazo-acetanilide).

3. The diazo-amido-compounds and phenyl iso-cyanate combine with urea derivatives.

In the preceding reactions the diazo-amido-bodies are not decomposed. This occurs very readily (4) on treating them with concentrated haloid acids; the diazo-amido-derivatives, like the diazo-benzol salts, then change to haloid benzols; the side products are salts of the bases previously in combination with the diazo-residue. Therefore the diazo-amido-compounds, in the presence of acids, are fully converted by nitrous acid into diazo-benzol salts. This method is not suitable for the determination of the constitution of unsym. diazo-amido-compounds, since it is ambiguous. Thus, on treating benzol-diazo-amido-p-toluol with dilute sulphuric acid, p-toluidin, phenol, and p-cresol are formed. The behaviour of the diazo-amido-bodies towards concentrated hydrofluoric acid, with the addition of diazo-piperidins, proved itself particularly well adapted for the preparation of fluoro-benzols (A. **243**, 220):

$$C_6H_5N{=}N.NC_5H_{10}+2HFl = C_6H_5Fl+N_2+HFl.HNC_5H_{10}.$$

5. Boiling water converts the diazo-amido-compounds into phenols and bases.

6. The reduction of the diazo-amido-bodies has not led to hydrazo-amido-derivatives—*e.g.* $C_6H_5NH{-}NH.NH.C_6H_5$; a decomposition into phenyl-hydrazin and aniline has been the regular result.

7. On boiling the alcoholic solution with sulphurous acid, the diazo-group is replaced by the sulpho-group:

$$C_6H_5N_2NHC_6H_5+2SO_2+2H_2O = C_6H_5SO_3H+N_2+C_6H_5NH_2.SO_3H_2.$$

11. Diazo-oxy-amido-compounds.

These compounds are formed (1) from diazo-compounds with β-alkyl- and alphyl-hydroxylamines (cp. B. **32**, 1546; A. **353**, 228); (2) from phenyl-hydrazins and nitroso-benzols, in the latter case with liberation of hydrogen. If α-alkylated phenyl-hydrazins are used; we get bodies like $C_6H_5N(CH_3)N\langle O \rangle NC_6H_5$ or $C_6H_5N(CH_3)N:N(:O)C_6H_5$, *i.e.* analogous to azoxy-compounds.

Diazo-oxy-amido-benzol $C_6H_5N_2.N(OH)C_6H_5$, m.p. 127°, yellowish needles of silky lustre, from nitroso-benzol with phenyl-hydrazin, or from diazo-benzol with phenyl-hydroxylamine.

Benzol-diazo-oxy-amido-methane $C_6H_5N_2.N(OH)CH_3$, m.p. 70°, from β-methyl-hydroxylamine and diazo-benzol chloride (B. **30**, 2278). Other compounds, see B. **32**, 3554; C. 1909, II. 18.

12. Diazo-imido-compounds.

The diazo-imido-compounds are ethers of hydro-nitric acid—hydrazoic acid. They are produced:

1. By the action of aqueous ammonia upon diazo-benzol perbromides:

$$C_6H_5N_2.Br_3+NH_3 = C_6H_5N\langle \begin{matrix} N \\ N \end{matrix} +3HBr.$$

2. By the action of hydroxylamine upon diazo-benzol sulphate (B. **25**, 372 ; **26**, 1271) :

$$C_6H_5N_2OSO_3H+NH_2OH = C_6H_5N_3+H_2O+SO_4H_2.$$

The hydroxylamines can sometimes be replaced by the salts of hydroxylamine-di-sulphonic acid (B. **33**, 3408).

3. By the action of sodium nitrite upon the hydrochloric acid solution of phenyl-hydrazin, when the nitroso-phenyl-hydrazins first produced lose water and form phenyl-diazo-imides :

$$C_6H_5N\begin{cases}NH_2\\NO\end{cases} = C_6H_5N\begin{cases}N\\N\end{cases}+H_2O.$$

4. From phenyl-hydrazin and diazo-benzol sulphate (B. **20**, 1528 ; **21**, 3415) :

$$\begin{matrix}C_6H_5NHNH_2\\C_6H_5N_2OSO_3H\end{matrix} \longrightarrow C_6H_5N\begin{cases}NH_2\\N:NC_6H_5\end{cases} \longrightarrow C_6H_5N\begin{cases}N\\N\end{cases}+C_6H_5NH_2.$$

5. Hydrazin and diazo-benzol sulphate yield, on the one hand, diazo-benzol-imide and ammonia ; upon the other, aniline and azo-imide or hydro-nitric acid, as by-products. These reactions are due to the breaking down of a non-accessible intermediate product, $C_6H_5N{=}N{-}NH.NH_2$ (B. **26**, 88, 1271) (cp. buzylene derivatives) :

$$NH_3+C_6H_5N_3 \longleftarrow C_6H_5N:N.NH.NH_2 \longrightarrow C_6H_5NH_2+N_3H.$$

6. By the action of sodium hypochlorite upon β-phenyl-semi-carbazide, the latter being first oxidised to phenyl-azo-carboxyl-amide, then transposed into diazo-benzol-amide, and finally converted into diazo-benzol-imide :

$$C_6H_5NH.NH.CONH_2 \longrightarrow C_6H_5N:N.CONH_2 \longrightarrow C_6H_5N:N.NH_2 \longrightarrow C_6H_5.N\begin{cases}N\\\|\\N\end{cases}$$

Analogous reactions are given by a number of substituted phenyl-semicarbazides (B. **40**, 3035).

7. By oxidation of diazo-benzol-amide with potassium hypobromite, or ammoniacal silver solution (B. **40**, 2388).

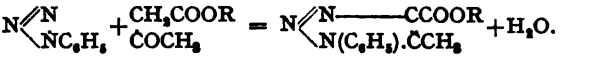
Diazo-benzol-imide, *phenyl-hydro-nitric ester* $C_6H_5N_3$, b.p. 59° (12 mm.), is a yellow oil with stupefying odour. It explodes at ordinary pressures if heated.

o-, m-, and p-Nitro-diazo-benzol-imide $NO_2C_6H_4N_3$, m.p. 52°, 55°, and 74°. **p-Bromo-diazo-benzol-imide**, m.p. 20° (B. **33**, 3409). **p-Amido-diazo-benzol-imide** $NH_2C_6H_4N_3$, m.p. 62°. **p-Bis-triazo-benzol, p-phenylene-bis-diazo-imide** $N_3C_6H_4N_3$, light-yellow plates, m.p. 83°, formed from acetyl-p-phenylene-diamine by the reactions (C. 1906, I. 1338) :

$$CH_3CONHC_6H_4NH_2 \longrightarrow CH_3CONHC_6H_4N_3 \longrightarrow NH_2C_6H_4N_3 \longrightarrow N_3C_6H_4N_3.$$

Transformations of the Diazo-benzol-imido-compounds.—(1) On boiling with HCl they decompose into nitrogen and chloraniline (B. **19**, 313). (2) On boiling with H_2SO_4 they split into nitrogen and amido-phenols (B. **27**, 192). (3) On boiling with alcoholic potash the diazo-benzol-imido-compounds are partly split into nitro-

phenols and hydro-nitric acid (B. **25,** 3328). (4) Heated by themselves, the ortho-nitrogenated diazo-imides are broken up into nitrogen and o-dinitro-benzols. (5) With methyl-magnesium iodide, and phenyl-magnesium bromide, diazo-benzol-imide form salts of diazo-amido-compounds, with splitting of the nitrogen ring. (6) With KCN, diazo-benzol-imide combines to form phenyl-cyano-triazene. (7) It combines additively with acetylene-dicarboxylic ester; with β-ketone-carboxylic ester, as well as malonic esters, it combines to form five-membered heterocyclic ring-systems, of the **triazol** group, water or alcohol being set free:



(8) By condensation of diazo-benzol-imide with benzaldehyde-aryl-hydrazones, **tetrazones** are formed (B. **40,** 2402), *e.g.* :

13. Azoxy-compounds.

Formation.—(1) By reduction of nitro- and nitroso-compounds with methyl or ethyl alcoholic potash solutions (B. **26,** 269) :

$$4C_6H_5NO_2+3HCH_2ONa = 2(C_6H_5N)_2O+3HCO_2Na+3H_2O.$$

Sodium amalgam and alcohol, zinc dust in alcoholic ammonia, and arsenious acid in alkaline solution (B. **28,** R. 125) reduce nitro-bodies to azoxy-compounds.

(2) By the oxidation of amido- and azo-derivatives (*Z. f. Ch.* 1866, 309; B. **6,** 557; **18,** 1420; **86,** 3805), as well as by the spontaneous oxidation of β-phenyl-hydroxylamine in the air. Nitroso-benzol is formed intermediately, and combines with unchanged β-phenyl-hydroxylamine to form azoxy-benzol (see Steric hindrance).

Behaviour.—(1) When reduced by heating with iron filings they yield azo-compounds; with ammonium sulphide, hydrazo-derivatives; and with acid reducing agents, amido-bodies, resulting from the decomposition and rearrangement of the hydrazo-compounds first produced. (2) Their rearrangement into oxy-azo-compounds, on digesting them with concentrated sulphuric acid, is interesting (Wallach and Belli, B. **18,** 525).

Azoxy-benzol, *azoxy-benzide* , m.p. 36°, forms long yellow needles, easily soluble in alcohol and ether, but not in water. It melts at 36°, and decomposes into azo-benzol and aniline when distilled. It is converted into p-oxy-azo-benzol by digestion with concentrated sulphuric acid, besides yielding other products (C. 1903, I. 324, 1082).

Concerning an isomeric azoxy-benzol, m.p. 84°, formed as a by-product of the reduction of nitroso-benzol with alcoholic soda solution, see B. **42,** 1364.

Benzene and H_2Cl_6, acting on azoxy-benzol, give benzene-azo-diphenyl $C_6H_5N_2C_6H_4.C_6H_5$ and diphenyl-azo-diphenyl (C. 1904, I. 1491).

o- and p-Nitro-azoxy-benzol, m.p. 49° and 149°. The o-compound on reduction gives *phenyl-azo-nitroso-* and *phenyl-azo-amido-benzol* (B. **32,** 3262). **Sym. o_2-dinitro-azoxy-benzol,** m.p. 175° (B. **36,** 3813). **Sym. p_2-dinitro-azoxy-benzol,** m.p. 192°, by oxidation of p_2-dinitro-azo-benzol. **Sym. m-dinitro-azoxy-benzol,** m.p. 141°, from m-dinitro-benzol (B. **25,** 608; **38,** 4013). **Sym. m-diamido-azoxy-benzol,** *azoxy-aniline,* m.p. 147° (B. **29,** R. 137). **p-Tetramethyl-diamido-azoxy-benzol,** m.p. 243°, from nitroso-dimethyl-aniline. **Trinitro-azoxy-benzols,** from azoxy-benzol (B. **23,** R. 104), **o-, m-, and p-Azoxy-toluol,** m.p. 59°, 38°, and 70°.

14. Azo-compounds.

Like the diazo-derivatives, these contain a group consisting of two nitrogen atoms; in the former the N_2 group is combined with only one benzene nucleus and an inorganic residue; here it is attached on either side to benzene nuclei, or to a benzene nucleus and an aliphatic radicle:

$C_6H_5—N=N—C_6H_5$	$C_6H_5—N=N—CH_3$
Azo-benzol	Benzol azo-methane.

In consequence, they are far more stable than the former, and do not react with the elimination of nitrogen.

Intermediate links between diazo- and azo-compounds are represented by the diazo-benzol cyanides, the benzol-azo-carboxylic derivatives, etc.

Classification and Nomenclature.—The true aromatic azo-bodies are distinguished as symmetrical, those in which the two residues are the same, and unsymmetrical, those in which the two residues are dissimilar. Mixed azo-bodies are those in which the azo-group joins an aromatic to an aliphatic radicle.

The names of the unsymmetrical azo-bodies are derived from the names of the two bodies in which the azo-group has replaced an atom of hydrogen each, separated by the word azo,—thus: $C_6H_5—N=N—C_6H_4N(CH_3)_2$, benzol-azo-dimethyl-aniline; $C_6H_5—N=N—CH_3$, benzol-azo-methane. Should the benzene residues contain substituents, the positions in the one residue are indicated by numbers 1 to 6, and in the second residue by numbers 1′ to 6′, with the understanding that the azo-group occupies the 1, 1′-position. Dis-azo- and tris-azo-compounds, containing two or three azo-groups, are known (B. **15,** 2812).

Formation.—1. By the moderated reduction of nitro-bodies in alkaline solution, because in acid solution the final reduction products of nitro-bodies, the amido-derivatives, are almost invariably produced. Azoxy-compounds are first formed, but by further reduction they pass into azo-derivatives. The reducing agents are:

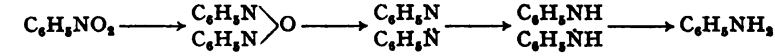
(*a*) Zinc dust in alcoholic potash or soda (B. **21,** 3139), or in ammonia.

(*b*) Sodium or magnesium amalgam and alcohol (C. 1904, II. 1383).

(*c*) Stannous chloride in sodium hydroxide (B. **18,** 2912).

Also (*d*) the electrolytic reduction of nitro-derivatives to azo-bodies (C. 1898, II. 775; 1900, I. 1175; 1901, II. 153).

By more complete reduction hydrazo-bodies are formed, along with the azo-derivatives; these can eventually be decomposed into amido-compounds. Azo-benzol is the middle member in the series of reduction products obtained from nitro-benzol, if β-phenyl-hydroxylamine is not taken into consideration:



Nitro-benzol Azoxy-benzol Azo-benzol Hydrazo-benzol Aniline.

2. By reduction of azoxy-compounds on heating them with iron filings.

3. By the oxidation (*a*) of hydrazo-bodies, and (*b*) of primary amido-derivatives in alkaline solution. This takes place in air alone (B. **42,** 2938), and more easily by means of potassium permanganate (A. **142,** 364), potassium ferricyanide or sodium hypobromite (B. **39,** 744).

4. By the action of nitroso-benzol upon aniline.

5. By the rearrangement of certain diazo-amido-bodies into amido-azo-derivatives.

6. By the transposition of certain diazo-amido-compounds into azo-amido-compounds.

7. By action of diazo-salts (*a*) upon tertiary anilines; (*b*) upon m-diamines; and (*c*) upon phenols.

The last two methods lead to amido-derivatives of the azo-hydrocarbons, some of which have become very important in the coal-tar colour industry.

Mixed azo-derivatives are frequently obtained by combining diazo-salts with suitable fatty bodies, *i.e.* such as contain easily replaceable hydrogen atoms in union with carbon, or with heterocyclic compounds like pyrrol, pyrazol, etc.

Properties.—The azo-bodies are more intensely coloured than the pale-yellow azoxy-derivatives. They unite with acids with great difficulty unless they contain an additional basic amido-group. They can be directly chlorinated, nitrated, and sulphonated. Reducing agents convert them into hydrazo-compounds, or decompose them at the point of double union, with the production of amido-compounds. The latter reaction serves to determine the constitution of the amido-azo-derivatives.

INDIFFERENT, SYMMETRICAL AZO-COMPOUNDS.—**Azo-benzol,** *azo-benzide* $C_6H_5N{=}NC_6H_5$, m.p. 68° and b.p. 293°, was discovered by Mitscherlich in 1834. It forms orange-red, rhombic crystals, readily soluble in alcohol and ether, but sparingly soluble in water. It is produced by the methods outlined above from nitro-benzol, aniline, and hydro-benzol. Azoxy-benzol yields it on distillation with iron filings (B. **207,** 329). It has also been obtained from potassium aniline by action of air, and from aniline and sodium (B. **10,** 1802). It is converted into benzidin by tin and hydrochloric acid; this is due to a transposition of the hydrazo-benzol first formed.

HCl in methyl-alcohol solution produces a fundamental change in azo-benzol, reduction and chlorination taking place simultaneously (A. **367,** 304). With benzol-sulphinic acid it combines to form phenyl-

sulphone-hydrazo-benzol. On heating with CS_2 *mercapto-thiazol* is produced (B. **24,** 1403).

Nitration of azo-benzol easily produces nitro-azoxy-benzols. **o-, m-, and p-Nitro-azo-benzol,** m.p. 71°, 96°, and 135°, are obtained by transformation of the three nitro-nitroso-benzols with aniline, or of the three nitranilines with nitroso-benzol (B. **36,** 3811, 3818). **2, 4-Dinitro-benzol-azo-benzol,** m.p. 117°, by oxidation of the hydrazo-benzol. **m_2- and p_2-Dinitro-azo-benzol,** m.p. 153° and 221°. **Trinitro-azo-benzols** (B. **32,** 3256). Sym. hexa-nitro-azo-benzol, m.p. 215° (B. **41,** 1297).

Reduction of o-nitro-azo-compounds produces phenyl-azimide oxides and phenyl-pseudo-azimides (*q.v.*) (B. **36,** 3822).

Azo-toluols.—o-Azo-toluol melts at 157°. m-Azo-toluol melts at 55°, and p-azo-toluol at 143° (B. **17,** 463; **18,** 2551). **Azoxylenes** and **azo-trimethyl-benzols** are known.

MIXED AZO-COMPOUNDS.—**Benzol-azo-methane,** *azo-phenyl-methane* $C_6H_5N{=}NCH_3$, b.p. about 150°, and **Benzol-azo-ethane** $C_6H_5.N{=}NCH_3.CH_3$, b.p. about 180°, are liquids with a peculiar odour. They are obtained by oxidising the corresponding hydrazins with mercuric oxide. Sulphuric acid transposes benzol-azo-ethane into the isomeric acetaldehyde-phenyl-hydrazone $C_6H_5NH.N : CH.CH_3$ (B. **29,** 794; **36,** 56). With amyl nitrite, and sodium alcoholate, both benzol-azo-ethane and acetaldehyde-phenyl-hydrazone give *benzol-azo-acet-aldoxime* $C_6H_5N : NC(NOH)CH_3$. In compounds of the type :

$$\begin{array}{lll} ArN : NC(NOH)R & \text{or} & ArNH.N : C(NO)R \\ ArN : NC(NOOH)R & \text{or} & ArNHN : C(NO_2)R \end{array}$$

the desmotropic relations between azo- and hydrazone forms are closer than in the simple mixed azo-bodies. These classes of bodies, designated as *benzol-azo-aldoximes* or *nitroso-phenyl-hydrazones*, and *benzol-azo-nitronic acids* or *nitro-phenyl-hydrazones*, respectively, are dealt with below, in connection with the related *amidrazones* and *formazyl* compounds.

Mixed azo-compounds are also produced by combination of diazo-salts and substances with a reactive CH_2 group. Thus we obtain benzol-azo-aceto-acetic ester with desmotropic hydrazone forms of the type $C_6H_5.NHN : C(COCH_3)(COOR)$. Concerning the structure of benzol-azo-amino-crotonic ester, see B. **35,** 1862.

Certain other bodies may also be regarded as mixed azo-compounds :—*Benzol-diazo-carboxylic acids* and their derivatives the *diazo-cyanides*, *diphenyl-sulpho-carbazone* and *carbo-diazone*, *benzoyl-diazo-benzol* (*q.v.*), and numerous azo-bodies produced by combination of diazo-salts with heterocyclic compounds like pyrrol, pyrazol, etc.

AMIDO-AZO-COMPOUNDS.—The indifferent azo-derivatives are all orange-yellow to orange-red in colour, but they are not dyes. By the introduction of amino- or HO groups in ortho- or para-position to the azo-group the resulting bodies, like o- and p-amido-azo-compounds, oxy-azo-compounds, and especially amido-azo-benzol-sulphonic acids, do become colours applicable in the dyeing of wool and silk (B. **35,** 4225). The number of azo-dyes is very great. Some of the simplest will be discussed in the following paragraphs, while the most important representatives of the class, technically speaking,

will be considered in other portions of this book, particularly in connection with the naphthalene group. The sulphonic acids of the amido-azo-bodies are of greater importance than the parent substances.

Formation.—1. From diazo-amido-compounds: p-amido-azo-benzol is obtained from diazo-amido-benzol. In the case of diazo-amido-benzol this transposition occurs on standing with alcohol, but more readily by the action of a slight quantity of aniline chlorohydrate.

This reaction only occurs readily if, in the reacting diazo-amido-compound, the position in the benzol nucleus adjacent to the amido-group in the para place be unoccupied.

However, compounds, like diazo-amido-p-toluol $CH_3[4]C_6H_4[1]N : N—[1']NHC_6H_4[4']CH_3$, in which the p-position with reference to the imido-group is occupied by CH_3, also suffer this transposition. It occurs on heating diazo-amido-p-toluol, dissolved in fused p-toluidin, to 65° with p-toluidin.

The amido-group of the resulting amido-azo-toluol occupies the o-position with reference to the diazo-group. It is o-amido-azo-toluol or [4]-*methyl-benzol-azo*-[4']-*methyl*-[2']-*amido-benzol* $CH_3[4]C_6H_4[1]N : N[1']C_6H_3[4']CH_3[2']NH_2$ (B. **17**, 77).

2. By the action of the diazo-compounds (*a*) upon the tertiary aromatic amines, or (*b*) upon m-diamines in neutral, or feebly acid, solution (B. **10**, 389, 654):

$$C_6H_5.N_2NO_3 + C_6H_5N(CH_3)_2 = C_6H_5.N : N.[1]C_6H_4[4]N(CH_3)_2 + NO_3H$$

$$C_6H_5.N_2NO_3 + C_6H_4\begin{cases}[1]NH_2\\[3]NH_2\end{cases} = C_6H_5.N : N.[1]C_6H_3\begin{cases}[2]NH_2\\[4]NH_2\end{cases} + NO_3H.$$

The first products with primary and secondary monamines, especially in neutral or acetic acid solution (B. **24**, 2077), are diazo-amido-compounds, which, under the previously mentioned conditions, are capable of rearranging themselves into amido-azo-derivatives.

But in the formation of diazo-amido-compounds from diazonium salts and nucleus-substituted anilines the isomeric amido-azo-compounds usually occur as by-products, and only become chief products in meta-substitutions, *e.g.* m-toluidin (*J. pr. Ch.* 2, **65**, 401).

The phenols act like the tertiary amines upon diazo-salts with the formation of oxy-azo-derivatives, which will be discussed later after the amido-phenols.

Properties and Behaviour.—The amido-azo-compounds are usually crystalline, and generally dissolve readily in alcohol. They are yellow, red, or brown in colour. With acids they form two isomeric series of salts: yellow unstable, and violet stable salts. The former are produced by the action of a defective quantity of acid upon amido-compounds, and easily pass into the darker isomeric salts by excess of acid, pressure, heat, etc. The dark salts are probably salts of the quinone-imide-hydrazone $C_6H_5NHN : C_6H_4 : NH.HCl$, and form the industrial amido-azo-dyes (B. **41**, 1171).

(1) Their decomposition upon reduction, and the great importance of this reaction, have been previously dwelt upon (B. **21**, 3471; C. 1908, I. 721). Occasionally decomposition, such as this, takes place on heating the bodies with hydrochloric acid (B. **17**, 395). If titanium trichloride is employed, the reduction splitting can be used for the

volumetric estimation of the dyes (B. **36,** 1552). (2) Amido-azo-compounds may be changed to diazo-azo-derivatives with nitrous acid. *Iso-dihydro-phene-tetrazins* may be obtained by reducing the diazo-salts of o-amido-azo-derivatives. (3) *Indulins* (*q.v.*) are produced on heating p-amido-azo-compounds with aniline hydrochloride, and *eurhodins* when o-amido-azo-bodies are employed. (4) When the o-amido-azo-compounds are oxidised they become *pseudo-azimido*-derivatives. (5) The o-amido-azo-compounds combine with aldehydes. Condensation products result, which are derived from *dihydro-pheno-triazin* (*q.v.*).

p-Amido-azo-benzol $C_6H_5.N:N[1]C_6H_4[4]NH_2$, yellow flakes or needles, m.p. 127°, b.p.$_{12}$. 225°, boils without decomposition even at ordinary pressures. It can be obtained from p-nitro-azo-benzol, and is prepared industrially by transposition of diazo-amido-benzol (B. **19,** 1953; **21,** 1633). MnO_2 and sulphuric acid oxidise it to quinone; reduction splits it into aniline and p-phenylene-diamine. With HCl it forms a bright-yellow and a deep-violet chlorohydrate. The latter was, like the oxalate, formerly used as a yellow dye. In the coal-tar industry it is used on a large scale as a fundamental material for obtaining diazo-dyes and indulins. While the salts of amido-azo-benzol are unimportant as dyes, the sulpho-acids, "acid yellow" or "real yellow," have valuable properties.

p-Acetamido-azo-benzol, m.p. 143°. **Benzol-azo-phenyl-cyanamide** $C_6H_5N:NC_6H_4NHCN$, m.p. 163°, obtained by the action of diazo-benzol chloride upon sodium cyano-aniline (C. 1906, II. 1054). **Benzol-azo-phenyl-glycin** $C_6H_5N:NC_6H_4NHCH_2COOH$, m.p. 140°, obtained from phenyl-glycin and benzol-diazonium chloride (B. **35,** 580). For further acidyl derivatives of p-amido-azo-benzol, see B. **35,** 1431; C. 1902, II. 360. **m-Amido-azo-benzol** $C_6H_5N_2[1]C_6H_4[3]NH_2$, m.p. 57°; its aceto-compound, m.p. 131°, has been obtained from nitroso-benzol and aceto-m-phenylene-diamine (B. **28,** R. 982). **Benzol-azo-p-dimethyl-aniline** $C_6H_5N:N[1]C_6H_4[4]N(CH_3)_2$, m.p. 116°. **p-Azo-benzol-trimethyl-ammonium iodide** $C_6H_5N:NC_6H_4N(CH_3)_3I$, m.p. 185°, obtained from benzol-azo-dimethyl-aniline with methyl iodide. Unlike the corresponding primary and tertiary amine salts, it does *not* dye wool and silk (A. **345,** 303). **Benzol-azo-diphenyl-amine,** *p-anilido-azo-benzol,* m.p. 82°. **o-Amido-azo-toluol** $CH_3[2]C_6H_4[1]N:N[1']C_6H_3[3',4'](CH_3)NH_2$, m.p. 100°, from o-toluidin. **m-Amido-azo-toluol** $CH_3[3]C_6H_4[1]N:N[1']C_6H_3[2',4'](CH_3)NH_2$, m.p. 80°. **m-Nitro-benzol-azo-p-amido-benzol,** m.p. 213° (B. **29,** R. 661).

2, 4-Diamido-azo-benzol $C_6H_5N_2C_6H_3(NH_2)_2$, m.p. 117°, small yellow needles, obtained from diazo-benzol nitrate and m-phenylene-diamine. Its HCl salt occurs in commerce under the name *chrysoïdin,* and dyes orange-red. On reduction it splits into aniline and unsym. triamido-benzol $C_6H_3(NH_2)_3$.

Sym. o$_2$-Diamido-azo-benzol $H_2N.C_6H_4.N_2.C_6H_4NH_2$, copper-red flakes, m.p. 134°, obtained by gentle oxidation of o-phenylene-diamine, with polymerisation of the o-quinone-di-imine first formed (B. **38,** 2348). The di-acetyl compound, m.p. 271°, is also obtained by reduction of o-nitro-acetanilide (B. **39,** 4062).

The **sym. p$_2$-Diamido-azo-benzol** $H_2N.C_6H_4.N_2.C_6H_4.NH_2$ has been obtained from nitro-acetanilide $NO_2.C_6H_4.NH.C_2H_3O$ by reduction

with zinc dust and alkali, and from the diazo-compound of mono-aceto-phenylene-diamine, with aniline (B. **18,** 1145); also by reduction of p_2-dinitro-azo-benzol (B. **18,** R. 628). It crystallises from alcohol in yellow needles, and melts at 241°.

The tetra-alkyl derivatives of p_2-diamido-azo-benzol form the so-called "azylins," first obtained by the action of nitric oxide upon dialkyl-aniline (B. **16,** 2768):

$$2C_6H_5.NR_2.R_2N.C_6H_4.N_2.C_6H_4.NR_2.$$

Also by the action of the diazo-compounds of dimethyl-p-phenylene-diamine upon tertiary anilines (B. **18,** 1143). The azylins are *red*, basic dyes, soluble in HCl with purple coloration, and in acetic acid with emerald-green coloration. By reduction with stannous chloride, or with tin and HCl, they are split into two molecules of dialkyl-p-phenylene-diamine. By heating with alkyl iodides (4 mol.) to 100° they are also split up, forming tetra-alkylised para-phenylene-diamine.

mm_1-Diamido-azo-benzol, m.p. 155°, and **Tetra-methyl-mm_1-diamido-azo-benzol,** m.p. 118°, obtained from m-nitraniline and m-nitro-dimethyl-aniline by reduction with zinc dust and alkali. In contrast with the o- and p-amido-azo-bodies, they are very feeble dyes (B. **35,** 4225).

3, 2', 4'-Tri-amido-azo-benzol $C_{12}H_{13}N_5 = H_2N.C_6H_4.N_2.C_6H_3\langle^{NH_2}_{NH_2}$, m.p. 144°, is best obtained from m-amido-phenylene-oxaminic acid $NH_2[1]C_6H_4[3]NH.CO.COOH$ by diazotising, combining with m-phenylene-diamine, and saponification. The action of nitrous acid upon m-phenylene-diamine itself produces a mixture of bases containing, besides tri-amido-azo-benzol, chiefly **Phenylene-disazo-m-phenylene-diamine** $C_6H_4[N_2C_6H_3(NH_2)_2]_2$, m.p. 116°–118°. The chlorides of this mixture of bases form the commercial *phenylene brown, Bismarck brown, Vesuvine,* or *Manchester brown,* which serves for dyeing cotton and leather (cp. B. **30,** 2203; **31,** 188).

15. Hydrazin Compounds.

The simplest aromatic hydrazin derivatives are: *Phenyl-hydrazin* $C_6H_5.NH.NH_2$; unsym. *diphenyl-hydrazin* $(C_6H_5)_2N.NH_2$, and sym. *diphenyl-hydrazin* $C_6H_5NH.NH.C_6H_5$, or *hydrazo-benzol.*

Phenyl-hydrazin and unsym. diphenyl-hydrazin both contain an NH_2 group. They show similar reactions in many respects, whereas the symmetrical diphenyl-hydrazin deports itself rather peculiarly. In the following paragraphs sym. diphenyl-hydrazin and its homologues, the *hydrazo-compounds,* the hydrazin derivatives longest known, will be placed at the head of the aromatic hydrazins. The hydrazo-compounds arrange themselves with the previously discussed azo-bodies, with which they possess genetic connections. Then will follow the mono-phenyl- and the unsym. diphenyl-hydrazin group.

Hydrazo-compounds.—Symmetrical diphenyl-hydrazin was discovered in 1863 by A. W. Hofmann upon reducing azo-benzol with care, and, inasmuch as it differed from the last compound in containing two hydrogen atoms more, it was called *hydrazo-benzol,* a name which has adhered to symmetrical diphenyl-hydrazin.

Formation.—Azo-benzol and allied compounds yield hydrazo-benzo, upon reducing them with alcoholic ammonium sulphide, with zinc dust, and with potassium or sodium amalgam. It is not necessary to isolate the azo-body; the proper nitro- and azoxy-derivatives can be treated with zinc dust and sodium hydroxide. Nitro-compounds can also be converted in alkaline solution into hydrazo-derivatives by electrolytic reduction (*Ch. Ztg.* **17**, 129, 209; C. 1898, II. 775).

Hydrazo-benzol, *sym. diphenyl-hydrazin* $C_6H_5NH.NHC_6H_5$, m.p. 131°, decomposes at higher temperatures; also on heating with alcohol to 120°–130° in azo-benzol and aniline. It forms colourless flakes or plates, insoluble in water, but easily soluble in alcohol and ether. It smells somewhat like camphor, and oxidises spontaneously in moist air, or in alcoholic solution, to azo-benzol, giving off H_2O_2, especially in the presence of alkali (B. **33**, 476; A. **316**, 331). Hydrazo-benzol is an indifferent body, forming no salts with mineral acids, but undergoing remarkable intramolecular atomic displacements (see Benzidin and semidin transposition, below). Strong reducing agents split up hydrazo-benzol into 2 mol. aniline. With nitro-benzol it transposes itself to azo-benzol and β-phenyl-hydroxylamine (B. **33**, 3508).

With phenyl iso-cyanate (B. **23**, 490) and phenyl-mustard oil (B. **25**, 3115) hydro-benzol gives urea derivatives; with aldehydes it gives various reactions: formaldehyde gives $CH_2(C_6H_5N.NHC_6H_5)_2$ and $CH_2\langle^{N(C_6H_5).N(C_6H_5)}_{N(C_6H_5).N(C_6H_5)}\rangle CH_2$; acetaldehyde $CH_3CH\langle^{NC_6H_5}_{NC_6H_5}$; while benzaldehyde oxidises hydrazo-benzol to azo-benzol (*J. pr. Ch.* 2, **65**, 97). On heating with CS_2 it yields sulpho-carbanilide and sulphur (B. **36**, 3841).

Mono-acetyl-hydrazo-benzol, m.p. 159°, decomposes at higher temperatures into azo-benzol and acetanilide. Di-acetyl-hydrazo-benzol, m.p. 105° (B. **17**, 379; A. **207**, 327). Further acetyl derivatives, see B. **31**, 3241; C. 1903, II. 359.

o-, m-, p-Methyl-hydrazo-benzol or **sym. o-, m-, p-Tolyl-phenyl-hydrazin** melt at 101°, 60°, and 86°.

Sym. hydrazo-toluols $CH_3C_6H_4NH.NHC_6H_4CH_3$: o-compound, m.p. 165°; m-compound, liquid (A. **207**, 116); p-compound, m.p. 128° (B. **9**, 829). **Hydrazo-xylols** (B. **21**, 3141).

Sym. di-halogen-substituted hydrazo-benzols are obtained from the corresponding azo-compounds. **p-Diamido-hydrazo-benzol,** *diphenin* $NH_2[4]C_6H_4[1]NH.NH[1']C_6H_4[4']NH_2$, m.p. 145°, from p-dinitro-azo-benzol with AmS_2 (B. **18**, 1136).

Unsym. nitro-hydrazo-benzols have been obtained by reduction of nitro-azo- and nitro-azoxy-compounds, and also from chloro-dinitro- and chloro-trinitro-benzol with phenyl-hydrazin (A. **190**, 132; **253**, 2; *J. pr. Ch.* 2, **37**, 345; **44**, 67; B. **32**, 3280; C. 1902, II. 41). **Sym. hexanitro-hydrazo-benzol,** black crystals of metallic lustre, m.p. 201°, from picryl chloride and hydrazin (B. **41**, 1295).

The Benzidin and Semidin Transposition of the Hydrazo-compounds.

Hydrazo-benzol undergoes a very remarkable rearrangement into an isomeric compound when it is treated with acids. When azo-benzol

is reduced in acid solution, the hydrazo-benzol which is produced does not form salts, but even in the cold is changed by mere contact with acids into a diamine, a diacid base : *benzidin* (*q.v.*) or *p-diamido-diphenyl.* Benzidin, a fundamental substance for the preparation of substantive cotton dyes, is prepared technically in this way. *Diphenylin*, an o-, p-diamido-diphenyl, occurs in small quantities besides benzidin (B. **17,** 1181) :

$$\begin{matrix} C_6H_4[4]NH_2 \\ C_6H_4[4]NH_2 \\ \text{Benzidin} \end{matrix} \longleftarrow \begin{matrix} C_6H_5NH \\ C_6H_5NH \\ \text{Hydrazo-benzol} \end{matrix} \longrightarrow \begin{matrix} C_6H_4[4]NH_2 \\ C_6H_4[2]NH_2 \\ \text{Diphenylin.} \end{matrix}$$

The chief transposition, in which the two amido-groups take up a para-position with respect to the junction of the two benzene nuclei, is called the *benzidin transposition* of the hydrazo-compounds.

The transposition is best effected by means of mineral acids, but benzidin, in the shape of its acidyl compounds, is also obtained from hydro-azo-benzol by boiling with formic, or acetic, acids (B. **35,** 1433).

Sym. o- and m-ditolyl-hydrazin or o- and m-hydrazo-toluol, as well as other hydrazo-compounds in which the p-hydrogen atoms of the imido-groups are free in both aromatic residues, yield with mineral acids the corresponding *p-diamido-ditolyls* or *tolidins*, etc.

If, however, p-hydrazo-toluol be treated with aqueous mineral acids, it changes in part to p-azo-toluol and p-toluidin, and partly to *o-amido-ditolyl-amine* (B. **27,** 2700). The latter body is principally formed by the action of stannous chloride and hydrochloric acid upon hydrazo-toluol :

$$CH_3\overline{\underline{H\ H}}\ HN{-}NH\ \overline{\underline{H\ H}}\ CH_3 \longrightarrow CH_3\ \overline{\underline{H\ H}}\ NH\ \overline{\underline{H\ CH_3}}\ H.$$

p-Hydrazo-toluene — o-Amido-[4, 3']-ditolyl-amine.

This is the *semidin* transposition ; it is so called because only the one NH group is converted into an NH_2 group, and not both NH groups, as in the *benzidin* transposition. In simple p-substituted hydrazo-benzols the amido-group can enter the o- or p-position with reference to the imido-group. Hence it is necessary to distinguish between an *o-* and *p-semidin* transposition.

Often these transpositions take place side by side, so that the semidin bases are obtained together with the diphenyl bases. Treated with HCl gas in benzene, hydrazo-benzol yields also small quantities of *o-amido-diphenyl-amine* (*Ch. Ztg.* **18,** 1095) :

$$H\ \overline{\underline{H\ H}}\ NH.NH\ \overline{\underline{H\ H}}\ H \longrightarrow H\ \overline{\underline{H\ H}}\ NH\ \overline{\underline{H\ \ \ H}}\ H.$$

With stannous chloride and HCl, p-acetamido-hydrazo-benzol passes into *aceto-p-diamido-diphenyl-amine* :

$$C_2H_3O.NH\ \overline{\underline{H\ H}}\ NH.NH\ \overline{\underline{H\ H}}\ H \longrightarrow C_2H_3O.NH\ \overline{\underline{H\ H}}\ NH\ \overline{\underline{H\ H}}\ NH_2.$$

When a substituent occupies the para-position in hydrazo-benzol, the benzidin transposition takes place with separation of this substituent. Thus, benzidin is produced by p-chloro-hydrazo-benzol and p-hydrazo-benzol-carboxylic acid. Concerning the influence of the substituents upon the transposition, see A. **369,** 1.

We may here make a brief survey of the transposition in which anilines substituted for the nitrogen become nucleus-substituted anilines, by a wandering of the substituents; this generally leads to a stronger basicity. These transpositions are: (1) that of phenyl-nitrosamines into p-nitroso-anilines (see above); (2) of phenyl-nitramines (diazo-benzolic acids) into p-nitraniline; (3) of β-phenyl-hydroxylamines into p-amido-phenols; (4) of phenyl-hydrazins into p-phenylene-diamines; (5) of chloryl-anilines into p-chloranilines; (6) of diazo-amides into p-amido-azo-bodies; (7) of hydrazo-benzols into benzidins and amido-diphenyl-amines, the formulæ being:

1. $C_6H_5N(CH_3)NO \rightarrow ONC_6H_4NHCH_3$
2. $C_6H_5NH.NO_2 \longrightarrow O_2NC_6H_4NH_2$
3. $C_6H_5NH(OH) \longrightarrow HOC_6H_4NH_2$
4. $C_6H_5NH(NH_2) \longrightarrow NH_2C_6H_4NH_2$
5. $C_6H_5NHCl \longrightarrow ClC_6H_4NH_2$
6. $C_6H_5NH(N_2C_6H_5) \rightarrow (C_6H_5N_2).C_6H_4NH_2$
7. $C_6H_5NHNHC_6H_5 \rightarrow NH_2C_6H_4.C_6H_4NH_2$ or $\rightarrow C_6H_5NH.C_6H_4NH_2$

To these are added a number of reactions in which carbon groups wander from nitrogen to the nucleus. Thus we have the transposition of phenyl-alkylamines into homologous anilines, of diacetanilide into acetamino-aceto-phenone, etc.; also the transpositions of phenyl-sulphaminic acid into o- and p-anilino-sulphonic acid, of phenyl-sulphuric acid, and phenyl-carbonic acid, into phenyl-sulphonic acid, and salicylic acid, respectively, as well as o-azo-compounds into oxy-azo-compounds (*q.v.*).

Phenyl-hydrazin Group.—Phenyl-hydrazin and unsym. diphenyl-hydrazin are formed in the reduction of diazo-benzol salts and diphenyl-nitrosamine, as well as from the reaction products formed when nitrous acid acts upon primary and secondary anilines:

$$\begin{array}{l} C_6H_5NH_2HCl \longrightarrow C_6H_5N : N.Cl \longrightarrow C_6H_5NHNH_2HCl \\ (C_6H_5)_2NH \longrightarrow (C_6H_5)_2N.NO \longrightarrow (C_6H_5)_2N.NH_2. \end{array}$$

Formation.—1. *By the reduction of diazo-salts*: (*a*) By the action of acid alkaline sulphites upon the diazo-derivatives. On allowing acid potassium sulphite to act upon the yellow potassium salt of diazo-benzol-sulphonic acid, colourless potassium phenyl-hydrazin sulphonate is formed:

$$C_6H_5—N=N—SO_3K + SO_3HK + H_2O = C_6H_5NH.NHSO_3K + SO_4KH.$$

When the sulphonate is heated with concentrated hydrochloric acid, phenyl-hydrazin chlorohydrate is produced, together with primary potassium sulphate:

$$C_6H_5.N_2.H_2.SO_3K + HCl + H_2O = C_6H_5.N_2H_3.HCl + SO_4KH.$$

The *sulphazides*—*e.g.* $C_6H_5.NH.NH.SO_2.C_6H_5$, *phenyl-benzene sulphazide*, or $C_6H_5N : NC_6H_4N_2H_2SO_3H$, azo-benzol-p-hydrazin-sulphonic acid—are prepared by the action of free sulphurous acid upon the acid solution of diazo-benzene salts.

p-Nitro-diazo-benzol nitrate and two molecules of potassium sulphite yield potassium p-nitro-phenyl-hydrazin disulphonate, $C_6H_4(NO_2)N(SO_3K)NH(SO_3K)$, which hydrochloric acid decomposes quantitatively into p-nitro-phenyl-hydrazin.

In the same manner dipotassium sulphite changes potassium ben-

zene-diazo-sulphonate into potassium phenyl-hydrazin disulphonate, $C_6H_5N(SO_3K)NH(SO_3K)$, which can be more easily obtained from nitroso-acetanilide and dipotassium sulphite. It is resolved by hydrochloric acid into phenyl-hydrazin and sulphuric acid, and decomposed by alkali into potassium benzene-diazo-sulphonate (B. **30,** 374).

(*b*) Potassium diazo-benzene sulphonate can be reduced with acetic acid and zinc dust.

(*c*) By the action of stannous chloride and hydrochloric acid upon the diazonium chlorides (B. **16,** 2976 ; **17,** 572) :

$$C_6H_5.N_2Cl+2SnCl_2+4HCl = C_6H_5.N_2H_3.HCl+2SnCl_4.$$

Diazo- and iso-diazo-benzol-alkali salts, when reduced with sodium amalgam, yield phenyl-hydrazin (B. **30,** 339).

2. Diazo-amido-bodies are reduced by zinc dust and acetic acid in alcoholic solution, and split into anilines and hydrazins:

$$\underset{\text{Diazo-amido-benzol}}{C_6H_5N_2.NH.C_6H_5} + 2H_2 = \underset{\text{Phenyl-hydrazin}}{C_6H_5.N_2H_3} + \underset{\text{Aniline.}}{NH_2.C_6H_5}$$

3. Nitrosamines, reduced by zinc dust and acetic acid, give unsym. alkyl-phenyl- or diphenyl-hydrazins ; aliphatic hydrazins (Vol. I.) have been similarly obtained :

$$\underset{\text{Diphenyl-nitroso-amine}}{(C_6H_5)_2N.NO}+2H_2 = \underset{\text{a-Diphenyl-hydrazin.}}{(C_6H_5)_2N.NH_2}+H_2O$$

Historical.—A. Strecker and Römer (1871), on treating diazo-benzol nitrate with acid potassium sulphite, obtained potassium phenyl-hydrazin sulphonate $C_6H_5NH.NHSO_3K$, and, on subjecting the diazide of sulphanilic acid to the same treatment, a soluble potassium salt, which, on boiling with HCl, yielded crystallising phenyl-hydrazin-p-sulphonic acid $C_6H_4\begin{cases}[1]NH—NH_2\\[4]SO_3H\end{cases}$, the first primary aromatic hydrazin compound. In 1875 Emil Fischer showed how to convert this body into phenyl-hydrazin chlorohydrate by boiling with HCl, and how to obtain, by means of alkaline hydroxide, the free phenyl-hydrazin, a body exceedingly capable of transposition (B. **8,** 589).

Properties.—The aromatic hydrazins are mono-acid bases, almost insoluble in water, but easily soluble in alcohol and ether. They boil at ordinary pressures with slight decomposition, and under low pressures without decomposition. In air they oxidise easily, assuming a brown coloration (C. 1907, II. 1067). They reduce Fehling's solution.

PHENYL-HYDRAZIN $C_6H_5NH—NH_2$, flat crystals, m.p. 19·6°, b.p. 241°–242°, $b.p._{12}$ 120°. Density at 21°, 1·091. Obtained by reduction of benzol-diazonium chloride. Also, in small quantities, on heating hydrazin hydrate with phenol to 220° (B. **31,** 2909). Its transpositions are described below. As one of the generators of *antipyrin* it has attained importance in industry, and it also serves as a reagent for aldehydes and ketones. This latter use is of special importance in the chemistry of hydrocarbons.

Phenyl-hydrazin chlorohydrate $C_6H_5NH.NH_2HCl$, brilliant white flakes, slightly soluble in concentrated HCl, yields p-phenylene-diamine

on heating to 200° with HCl. Carboxylates, see B. **27,** 1521. **Sodium phenyl-hydrazin** $C_6H_5NNa.NH_2$, obtained by dissolving sodium in phenyl-hydrazin. It forms a reddish-yellow, amorphous mass, which, with halogen alkyls and haloids, forms the so-called α-phenyl-hydrazin derivatives (B. **19,** 2448 ; **22,** R. 664).

Potassium Phenyl-hydrazin (B. **20,** 47).

Substituted Phenyl-hydrazins (A. **248,** 94 ; B. **22,** 2801, 2809).—**p-Chloro-phenyl-hydrazin,** m.p. 83°. **p-Bromo-phenyl-hydrazin,** m.p. 106°. **p-Iodo-phenyl-hydrazin,** m.p. 103°. **o-Nitro-phenyl-hydrazin,** m.p. 90°, brick-red needles (B. **27,** 2549). **o-Nitro-s-formyl-phenyl-hydrazid,** m.p. 177° (B. **22,** 2804).

For hetero-ring formation from these o-nitro-compounds, see below.

p-Nitro-phenyl-hydrazin, m.p. 157°, is often useful for separating and characterising aldehydes and ketones (B. **32,** 1806). 2, 4-*Dinitro-phenyl-hydrazin*, yellow prisms, m.p. 197°, from dinitro-bromo-benzol and hydrazin hydrate (C. 1908, I. 125).

Homologous Phenyl-hydrazins.—**o-Tolyl-hydrazin,** m.p. 59°. **m-Tolyl-hydrazin,** liquid. **p-Tolyl-hydrazin,** m.p. 61°. **p-Xylyl-hydrazin,** m.p. 78°. **Pseudo-cumyl-hydrazin** (A. **212,** 338 ; B. **18,** 3175 ; **22,** 834 ; C. 1905, II. 40).

Unsym. diphenyl-hydrazin $(C_6H_5)_2N.NH_2$, m.p. 34°, b.p.$_{50}$ 220°, obtained by reduction of diphenyl-nitrosamine, forms, with glucose, diphenyl-hydrazones, soluble with difficulty. By oxidation with ferric chloride it passes into tetraphenyl-tetrazone.

Triphenyl-hydrazin $(C_6H_5)_2N.NHC_6H_5$, obtained by the action of phenyl-magnesium bromide upon β-phenyl-hydroxylamine. By alcoholic HCl it is transposed into N-phenyl-benzidin $C_6H_5NH.C_6H_4.C_6H_4.NH_2$ (B. **40,** 2099).

Tetraphenyl-hydrazin $(C_6H_5)_2N.N(C_6H_5)_2$, m.p. 144°, by oxidation of diphenyl-amine with MnO_4K or PbO_2 ; also from sodium diphenyl-amine $(C_6H_5)_2N.Na$ with iodine (B. **39,** 1501). It dissolves in concentrated H_2SO_4 with a deep-blue colour, being partly transposed into NN'-diphenyl-benzidin $C_6H_5NH.C_6H_4.C_6H_4.NHC_6H_5$ (cp. C. 1907, I. 406). HCl splits it into diphenyl-amine and p-chloraniline-triphenyl-amine, a reaction in which diphenyl-chloramine $(C_6H_5)_2NCl$ must be assumed as an intermediate product (B. **41,** 3508).

Tetra-p-tolyl-hydrazin $(CH_3.C_6H_4)_2N.N(C_6H_4CH_3)_2$, m.p. 136°, by oxidation of p-ditolyl-amine with MnO_4K, and by heating tetra-p-tolyl-tetrazone. It combines with acids, halogens, metalloid and metallic chlorides like PCl_5, $SbCl_3$, $SnCl_4$, etc., to form deep-violet addition products, resembling salts, from which water regenerates the unchanged hydrazin. In neutral solvents these partly very unstable compounds soon decompose to form p-ditolyl-amine, and derivatives of ditolyl-hydroxylamine $(CH_3C_6H_4)_2NOH$, which, however, undergo an immediate further change, with formation of derivatives of di-tertiary dihydro-phenazin (B. **41,** 3478).

Behaviour of the Phenyl-hydrazins.—(1) While the phenyl-hydrazins are pretty stable towards reducing agents, they may be readily reconverted into diazo-compounds by moderate oxidation ; this is effected by the action of mercuric oxide upon their sulphates or sulphonates.

When boiled with copper sulphate, ferric chloride, potassium chromate, Caro's acid, or sodium hypochlorite (C. 1909, II. 596), the

phenyl-hydrazins throw off nitrogen and become benzols—this reaction will also serve for the replacement of the diazo-group by hydrogen and by the halogens if the free phenyl-hydrazin be replaced by chlorine, bromine, or iodine (B. **18,** 90, 786; **25,** 1074; C. 1908, II. 1022). The liberated nitrogen also answers for the quantitative estimation of the hydrazins.

The phenyl-hydrazins also reduce Fehling's solution (B. **26,** R. 234). Consult B. **28,** R. 996; **29,** R. 977, for additional reduction reactions with phenyl-hydrazin.

(2) Sodium liberates hydrogen, and α-sodium phenyl-hydrazins result.

(3) Nitrous acid converts the phenyl-hydrazins into nitroso-hydrazins.

(4) Halogen alkyls replace the imido- and amido-hydrogen of the phenyl-hydrazins, and eventually form phenyl-hydrazonium compounds.

(5) Acid radicles may also thus be easily introduced into phenyl-hydrazins.

(6) Chlorine and bromine, at low temperatures, convert the primary phenyl-hydrazins into the corresponding diazonium salts. At higher temperatures, and in the presence of mineral acids, we get halogen phenyl-hydrazins with nuclear substitution (C. 1908, I. 2149; 1909, II. 595).

(7) The aldehydes and ketones combine with the phenyl-hydrazins, usually with the immediate separation of water and formation of *phenyl-hydrazones*. This reaction, like the oxime formation, is characteristic of the aldehydes and ketones.

(8) When the phenyl-hydrazins are heated to 200° with fuming hydrochloric acid, they are transposed into para-phenylene-diamines (B. **28,** 1538).

PHENYL-ALKYL-HYDRAZINS.—The unsymmetrical compounds, with an alkyl residue, are called "α"-compounds, and the symmetrical ones "β"-compounds.

Modes of Formation.—(1) Both isomers are generated by the action of alkyl bromides upon phenyl-hydrazin (A. **199,** 325; B. **17,** 2844). The isolation of the β-compounds is based upon their capacity of passing into azo-compounds by oxidation with HgO. These, owing to their volatility, and their indifference towards acids, can easily be separated from the other products, and can then be converted by reduction back into the original β-alkyl-phenyl-hydrazins. The α-compounds are formed (2) by the action of alkyl bromides upon sodium-phenyl-hydrazin (B. **19,** 2450; **22,** R. 664); (3) by the reduction of the corresponding nitrosamines with zinc dust; (4) by treatment of β-aceto-phenyl-hydrazin $C_6H_5NH.NHCOCH_3$ with halogen compounds, and saponification with boiling dilute acids (B. **26,** 946).

α-Methyl-phenyl-hydrazin $C_6H_5N(CH_3)NH_2$, b.p.$_{35}$ 131°, by transposition gives methyl-p-phenylene-diamine. **α-Ethyl-phenyl-hydrazin** $C_6H_5N(C_2H_5)NH_2$, b.p. 237°. Both compounds on oxidation give tetrazone (*q.v.*). The ethyl compound combines with ethyl bromide to form **Diethyl-phenyl-hydrazonium bromide** $C_6H_5N(C_2H_5)_2BrNH_2$, which, on reduction, gives diethyl-aniline.

α-Propyl-, α-Isopropyl-, α-Isobutyl-, α-Isoamyl-phenyl-hydrazin boil at 247°, 236°, 245°, 262° (B. **30,** 2809). **α-d-Amyl-phenyl-hydrazin**

$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!CH.CH_2N(C_6H_5).NH_2$, b.p.$_{50}$ 173°–175°, has been used for the direct splitting up of racemic aldehydes and ketones (B. **38,** 868).

Ethylene-phenyl-hydrazin $C_6H_5N(NH_2)C_2H_4.N(NH_2)C_6H_5$, m.p. 90° (B. **21,** 3203; A. **310,** 156). Unsym. **o-Amido-phenyl-methyl-hydrazin** $NH_2[2]C_6H_4[1]N(CH_3)NH_2$, an easily resinified oil, is produced from nitro-nitroso-methyl-aniline by reduction with alcoholic Am_2S.

HETERO-RING FORMATIONS OF O-SUBSTITUTED PHENYL-HYDRAZINS.—On boiling with an alkaline hydrate, o-nitro-phenyl-hydrazin passes into azimidol (*q.v.*). The formyl compound of o-nitro-phenyl-hydrazin yields α-pheno-triazin on reduction with sodium amalgam and acetic acid. The unsym. o-amido-phenyl-methyl-hydrazin, when treated with HNO_2, passes into pheno-methyl-hydro-tetrazin :

$$C_6H_4\begin{cases}[1]NH.NH_2\\[2]NO_2\end{cases} \xrightarrow{KOH} C_6H_4\begin{cases}[1]N=N\\[2]N(OH)\end{cases}$$ Azimidol

$$C_6H_4\begin{cases}[1]NH.NHCHO\\[2]NO_2\end{cases} \xrightarrow{H} C_6H_4\begin{cases}[1]N=N\\[2]N=CH\end{cases}$$ α-Pheno-triazin

$$C_6H_4\begin{cases}[1]N(CH_3).NH_2\\[2]NH_2\end{cases} \xrightarrow{NOOH} C_6H_4\begin{cases}[1]N(CH_3).N\\[2]NH\text{——}N\end{cases}$$ Pheno-methyl-dihydro-tetrazin.

β-Methyl- and **β-ethyl-phenyl-hydrazin** are colourless oils, oxidising, in air, to *benzol-azo-methane* and *-ethane*, from which they can be recovered by reduction. β-Methyl-phenyl-hydrazin is also obtained from *antipyrin* (*q.v.*) by boiling with alcoholic potash (B. **39,** 3265). **β-Alkyl-phenyl-hydrazin,** b.p.$_{110}$ 177° (B. **22,** 2233).

Di- and **tri-alkylated phenyl-hydrazins** are prepared from the sodium compound of *α-methyl-phenyl-formyl-hydrazin* $C_6H_5N(CH_3)N.NaCHO$ with alkylene iodide, the formyl group being detached by means of fuming hydrochloric acid. The dialkylated phenyl-hydrazins, under the action of alkylene iodide, give rise to quaternary azonium compounds, *e.g.* $C_6H_5N(CH_3)_2I.NH.CH_3$, besides trialkyl-phenyl-hydrazins. **α-β-Dimethyl-phenyl-hydrazin** $C_6H_5N(CH_3).NH.CH_3$, b.p. 93°; **α, β-Di-ethyl-phenyl-hydrazin** $C_6H_5N(C_2H_5)NHC_2H_5$, b.p.$_{11}$ 111°–115°, are produced by the action of zinc methyl and zinc ethyl upon benzol-diazonium chloride (B. **35,** 4179). **Phenyl-trimethyl-hydrazin,** b.p.$_8$ 93° (B. **27,** 696).

PHENYL-HYDRAZONE AND OSAZONE.—As the aldehydes and ketones yield oximes with hydroxylamines, so with phenyl-hydrazin they pass into *phenyl-hydrazones*. The compounds derived from the aldehydes are also called "*aldehydrazones*" (A. **247,** 194, footnote), the ketone derivatives "*keto-hydrazones*," and the dihydrazones of the α-dicarbonyl compounds "*osazones*" (B. **21,** 984; **41,** 73) :

$$R'.CHO+NH_2NHC_6H_5 = R'.CH : N.NHC_6H_5+H_2O$$
$$(R')_2CO+NH_2NHC_6H_5 = (R')_2C : N.NHC_6H_5+H_2O.$$

The osazones are also formed from the α-oxy-aldehydes and α-oxy-ketones, hydrazones being formed first, in which the alcohol group, adjoining the aldehyde, or keto, group, is oxidised by the excess of phenyl-hydrazin to a CO group :

$$RCHOH.CHO+3C_6H_5NH.NH_2 = RC(:N.NHC_6H_5)CH : N.NHC_6H_5 + C_6H_5NH_2+NH_3.$$

The formation of osazones has acquired a special importance in the chemistry of sugars (Vol. I.).

Of the phenyl-hydrazones, of the aldehydes and ketones, numerous isomeric forms have been discovered, and their occurrence is, as in the case of the oximes, attributed to a cis-trans-isomerism. The first isomeric osazones were found in 1895, through the action of phenyl-hydrazin upon dioxo-succinic ester (Vol. I.), three forms being discovered (B. **28,** 64). But no definite evidence as to configuration resulted.

The monoximes of α-aldehyde-ketones and α-diketones, treated with phenyl-hydrazin, yield *hydrazoximes.* Thus, from methyl-glyoxalic oxime we obtain methyl-glyoxal-oxime: **Methyl-glyoxal-phenyl-hydrazoxime** $CH_3C(:NNHC_6H_5)CH:NOH$, m.p. 134° (A. **262,** 278).

When phenyl-hydrazones are formed, an addition product is probably first generated, corresponding, in its constitution, to ammonia aldehyde. In a few cases, *e.g.* those of oxalic acid ester and dioxo-succinic ester, addition products have been identified, which easily pass into phenyl-hydrazones with elimination of water:

$$\begin{matrix} CO_2C_2H_5.CO \\ | \\ CO_2C_2H_5.CH_2 \end{matrix} + NH_2NHC_6H_5 = \begin{matrix} CO_2C_2H_5C\langle \begin{matrix} NH—NHC_6H_5 \\ OH \end{matrix} \\ | \\ CO_2C_2H_5CH_2 \end{matrix}$$

$$\begin{matrix} CO_2C_2H_5.CO \\ CO_2C_2H_5.CO \end{matrix} + 2NH_2NHC_6H_5 = \begin{matrix} CO_2C_2H_5C\langle \begin{matrix} NH—NHC_6H_5 \\ OH \end{matrix} \\ | \\ CO_2C_2H_5C\langle \begin{matrix} NH—NHC_6H_5. \\ OH \end{matrix} \end{matrix}$$

The fact that dioxo-succinic ester gives an addition compound tells in favour of the ammonia-aldehyde view, and against the ammonium-salt view, suggested by the case of oxalic ester (A. **295,** 339). Phenyl-hydrazin-p-sulphonic acid seems only to yield addition products of the formula $RCH(OH)NHNHC_6H_4SO_3H$ with the aldehydes (B. **35,** 2000).

Since the phenyl-hydrazones are characteristic of the corresponding compounds containing aldehyde and ketone groups, they had to be repeatedly mentioned, in advance, in dealing with aliphatic compounds, and we shall deal with them again in connection with the aromatic compounds in which aldehyde and ketone groups are present. It seems, however, advisable to refer briefly to the aliphatic phenyl-hydrazone derivatives. The following have received mention in the first volume of this work:—Phenyl-hydrazones of the simple aldehydes; of the simple ketones; of the diketones; of glyoxylic acid; of pyro-racemic acid; of aceto-acetic ester; of lævulinic acid; of mesoxal-aldehyde; of acetone-oxalic ester; of mesoxalic acid; of oxal-acetic ester; of acetone-dicarboxylic ester; of acetone-diacetic acid; of tetroses; of oxalyl-diacetone; of dioxo-succinic acid; of oxalo-succinic ester; of arabinose; of rhamnose; of the glucoses; of milk sugar; of maltose and isomaltose.

Formation of the Phenyl-hydrazones.—(1) By the action of phenyl-hydrazin and unsym. alkyl-phenyl- or unsym. diphenyl-hydrazin upon aldehydes and ketones (see above). (2) By the addition of phenyl-hydrazin to trebly linked carbon atoms; the phenyl-hydrazone of

oxalo-acetic ester is also produced by the addition of phenyl-hydrazin to acetylene-dicarboxylic ester :

$$\begin{matrix} CO_2.C_2H_5.C \\ \| \\ CO_2.C_2H_5.C \end{matrix} + NH_2NHC_6H_5 = \begin{matrix} CO_2.C_2H_5.C{=}N.NH.C_6H_5 \\ | \\ CO_2.C_2H_5.CH_2 \end{matrix}$$

(3) By the interaction of diazo-benzol salts and many aliphatic bodies, containing hydrogen atoms readily replaceable by alkali metals—*e.g.* malonic ester and aceto-acetic ester :

$$(CO_2C_2H_5)_2CH_2 + C_6H_5{-}N_2OH = (CO_2C_2H_5)_2C{=}N{-}NH.C_6H_5 + H_2O$$

Phenyl-hydrazone-mesoxalo-ester

$$\begin{matrix} CO_2C_2H_5CH_2 \\ | \\ CH_3.CO \end{matrix} + C_6H_5{-}N_2OH = \begin{matrix} CO_2C_2H_5C{=}N{-}NHC_6H_5 \\ | \\ CH_3.CO \end{matrix} + H_2O$$

Phenyl-hydrazone-aceto-glyoxylic ester.

The examination of desmotropic forms, in which the enol- and the keto-forms can be isolated, has shown that only the former reacts with diazonium salts. We must therefore assume that, in all cases, the azo group tackles the enol hydroxyl, forming O-azo-compounds, which transpose themselves into C-azo-compounds and then into phenyl-hydrazones (B. **41,** 4012). In some cases (see Tribenzoyl-methane) the isolation of the various intermediate products has been accomplished.

The body obtained from malonic ester with diazo-benzol hydrate is identical with that obtained from mesoxalic ester and phenyl-hydrazin. For the compound obtained from acetic acid ester, and diazo-benzol salts, we may have to replace the hydrazone formula $C_6H_5NHN : C(COCH_3)CO_2C_2H_5$ by the desmotropic formula of a **benzol-azo-aceto-acetic ester** $C_6H_5N : N.CH(COCH_3)CO_2C_2H_5$, since in dilute sodium hydrate the ester dissolves into a salt from which CO_2 precipitates the ester without change—a behaviour which is best explained by the presence of one of the mobile H atoms of the aceto-acetic ester (B. **32,** 197 ; A. **312,** 128). On the other hand, benzol-azo-aceto-acetic ester is converted into the hydrazone of pyro-racemic aldehyde by saponification and liberation of CO_2. This involves a transposition, for the pyro-racemic aldehydrazone, treated with chloro-acetic ester and sodium ethylate, yields an ester which, on reduction, yields anilido-acetic acid. The latter is only possible if the residue of the chloro-acetic acid was connected with the N atom to which the phenyl group had been attached (A. **247,** 190).

The product of the combination of cyanacetic ester and diazo-benzol salts occurs in two forms—the α-form, m.p. 125°, and the β-form, m.p. 85°, which are regarded as stereo-isomeric hydrazone forms $C_6H_5NH.N : C(CN)COOR$. Alkali easily converts the β-form into the α-form (B. **38,** 2266). Glutaconic ester (Vol. I.) reacts with 2 mol. of diazo-benzol salts, with formation of compounds containing the phenyl-hydrazone group as well as the azo-group $CO_2R.C : (N.NHC_6H_5).CH : C.(N : NC_6H_5)CO_2R$ (B. **40,** 4928). Concerning the constitution of the reaction products of diazo-benzol salts upon amino-crotonic ester, etc., see B. **36,** 1449.

The tendency towards the formation of phenyl-hydrazones is so-

great that CO_2 is split off from alkyl-aceto-acetic acids by diazo-benzol chloride, with formation of the phenyl-hydrazone of an α-diketone; and from alkyl aceto-acetic esters, with elimination of the acetyl group, phenyl-hydrazones of α-ketone-carboxylic esters are formed:

$$\begin{matrix}CH_3.CH.CO_2H \\ CH_3.CO\end{matrix} + C_6H_5N_2Cl = \begin{matrix}CH_3.C : N.NHC_6H_5 \\ CH_3CO\end{matrix} + CO_2 + HCl$$

Diacetyl-phenyl-hydrazone (Vol. I.)

$$\begin{matrix}CH_3.CH.CO_2C_2H_5 \\ CH_3.CO\end{matrix} + C_6H_5N_2Cl + H_2O = \begin{matrix}CH_3C.CO_2C_2H_5 \\ N.NHC_6H_5\end{matrix} + CH_3CO_2H + HCl$$

Phenyl-hydrazone-pyro-racemic ester.

From malonic acid and diazo-benzol chloride, also, glyoxylic phenyl-hydrazone is formed and CO_2 split off (C. 1905, I. 1538). On rules of rejection of acidyl groups from di-acidyl-acetic esters by diazo-benzol salts, see B. **35,** 915. The latter act like HNO_2, which produces oximes under similar conditions (Vol. I.).

Transformations of the Phenyl-hydrazones.—On heating the phenyl-hydrazones with dilute mineral acids they break up into their progenitors. By careful reduction many phenyl-hydrazones have been converted into phenyl-hydrazido-compounds (B. **28,** 1223; **30,** 736; C. 1899, I. 560). The phenyl-hydrazones often unite with HCN even more easily than do aldehydes and ketones to form cyano-hydrins, or nitriles of α-phenyl-hydrazido-carboxylic acids (B. **33,** 3550).

Very few classes of organic compounds are capable of entering into the formation of heterocyclic bodies to the extent manifested by the hydrazin derivatives, whose intramolecular condensation reactions are, therefore, of the utmost importance in the development of the chemistry of ring-systems containing nitrogen. Some of the most important condensations have been met with in connection with the phenyl-hydrazones of the fatty compounds, and will be again given in condensed form, while others will receive mention at the conclusion of the acid hydrazides.

1. *Indols* result upon heating the phenyl-hydrazones of aldehydes, ketones, and ketonic acids with zinc chloride, stannous chloride, or mineral acids.

2. *Pyrazolins* result from the transposition of the phenyl-hydrazones of α-olefin aldehydes and ketones.

3. *Oso-tetrazones* are produced when the osazones or α-diphenyl-hydrazones of α-dialdhydes, α-aldehyde-ketones, and α-diketones are oxidised.

4. Boiling acids change the α-osazones and oso-tetrazones to *oso-triazoles.*

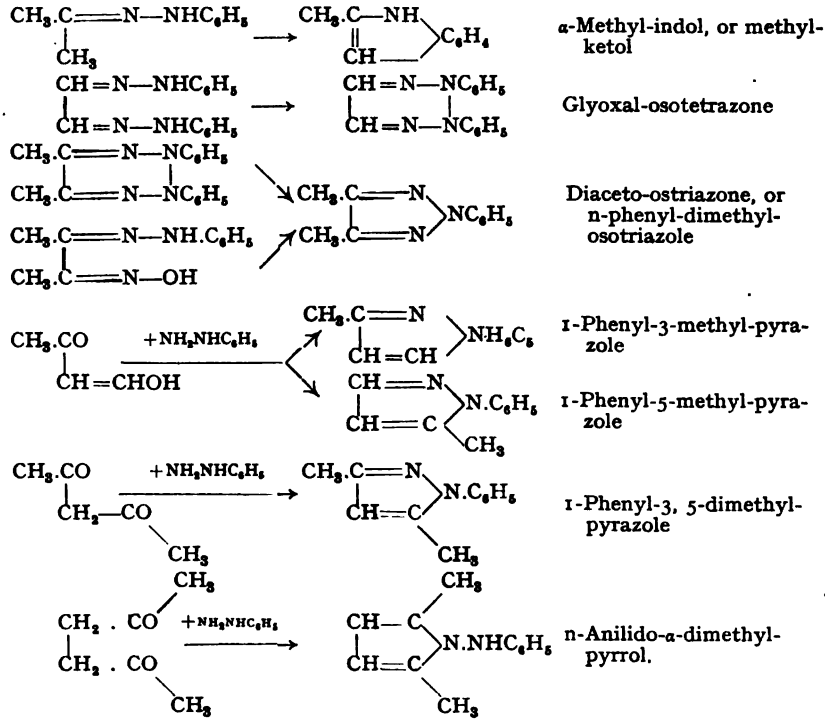
5. Dehydrating agents convert α-hydrazoximes into *oso-triazoles.*

6. *Pyrazoles* result from the phenyl-hydrazones of the 1, 3-oxy-methylene ketones, and β-diketones, by the exit of water; they are ring-shaped nitrogen derivatives of the 1, 3-olefin ketones.

7. The phenyl-hydrazones of 1, 4-diketones rearrange themselves into *n-anilido-pyrrols.*

In preparing ring-shaped condensation products of the hydrazones the latter have frequently not been isolated, but simply worked over.

The following scheme represents the hetero-ring-formations possible with the phenyl-hydrazones :



PHENYL-HYDRAZIN DERIVATIVES OF INORGANIC ACIDS.—**Thionyl-phenyl-hydrazone** $C_6H_5NH.N{=}SO$, melting at 105°, consists of sulphur-yellow coloured prisms. It is obtained, like the *thionyl-alkylamines* and *thionyl-anilines*, by the interaction of thionyl chloride and phenyl-hydrazin. All phenyl-hydrazins having a free amido-group yield thionyl-phenyl-hydrazones when acted upon with thionyl chloride (B. **27,** 2549). Thionyl-phenyl-hydrazone is more easily produced when thionyl-aniline acts upon phenyl-hydrazin. Further, it results upon gently digesting *phenyl-hydrazin-sulphinic acid* $C_6H_5NH.NH.SOOH$, obtained from sulphur dioxide and phenyl-hydrazin (B. **28,** 474). Thionyl chloride, acetyl chloride, and other acid chlorides rearrange thionyl-phenyl-hydrazin into *diazo-benzol chloride*, in that it reacts as if it were *diazo-benzol sulphoxide* $C_6H_5N{=}N.S(OH)$ (A. **270,** 114).

Phenyl-hydrazin-sulphonic acid $C_6H_5NH.NH.SO_3H$.—The potassium salt is formed in the reduction of potassium benzene-diazo-sulphonate with sulphuric acid or monalkali sulphites. For the behaviour of the potassium salt towards mineral acids, and the rôle it plays in the history of the discovery of phenyl-hydrazin, see above.

p-Nitro-phenyl-hydrazin-disulphonic acid $C_6H_4(NO_2)N(SO_3H)NH(SO_3H)$.—Its *dipotassium salt* consists of sulphur-yellow needles, formed on adding an excess of a sulphite solution to nitro-diazo-benzol ester, nitrate, or potassium iso-diazo-benzol. Hydrochloric acid

resolves it into p-nitro-phenyl-hydrazin, and it dissolves in an excess of potash to a red *tripotassium salt* $C_6H_4(NO_2)N(SO_3K)NK(SO_3K)$ (B. **29,** 1830).

Azo-benzol-phenyl-hydrazin-sulphonic acid $C_6H_5N:N.C_6H_4NH.NHSO_3H$, in purple needles decomposing even below 100°, is formed by the action of SO_2 upon a concentrated solution of diazo-benzol sulphate. With aldehydes it condenses to hydrazones, splitting off the sulpho-group (C. 1909, I. 355).

Phenyl-benzol-sulphazide $C_6H_5NH.NH.SO_2C_6H_5$, m.p. 148°–150°, formed from phenyl-hydrazin and benzol sulpho-chloride in ether, and from a diazo-benzo-salt solution with SO_2 or Na hydrosulphite (B. **20,** 1238; **40,** 422).

For the action of PCl_3, $POCl_3$, $PSCl_3$, $AsCl_3$, BCl_3, $SiCl_4$ upon phenyl-hydrazin, see A. **270,** 123.

CARBOXYLIC ACID DERIVATIVES OF PHENYL-HYDRAZIN.—Acid residues of the most varied character can be as readily introduced into phenyl-hydrazin, and generally by the same methods, as into aniline. The domain of the bodies thus won from phenyl-hydrazin is scarcely less extensive than that of the acid derivatives of aniline, and in the multiplicity of phenomena really surpasses it.

The acid hydrazides and the hydrazido-acids have shown themselves to be as well adapted as the phenyl-hydrazones for the formation of heterocyclic derivatives. Each group of carboxylic derivatives of phenyl-hydrazin will be followed by the most important hetero-ring formations, arranged in tabular form, which will later be discussed in a different connection in the section devoted to "heterocyclic compounds."

The *nitro-hydrazones*, *amidrazones*, and *formazyl derivatives* will receive attention at the conclusion of the simpler carboxylic derivatives of phenyl-hydrazin.

Fatty Acid Derivatives.—The fatty acid residues enter the amido-group of phenyl-hydrazin very readily with the production of sym. or β-acidyl compounds. The unsym. or α-acidyl compounds are made (1) by the action of acid chlorides or anhydrides upon sodium phenyl-hydrazin (B. **22,** R. 664); (2) by action of suitable haloid derivatives upon β-acetyl-phenyl-hydrazin, and subsequent splitting off of the β-aceto-group on boiling with dilute sulphuric acid, when the group occupying the α-position will not be attacked (B. **26,** 945).

The sym. phenyl-hydrazides, treated with ferric chloride and concentrated sulphuric acid, yield reddish to bluish violet colours, whereas the unsym. bodies are not coloured (B. **27,** 2965, Bülow's reaction).

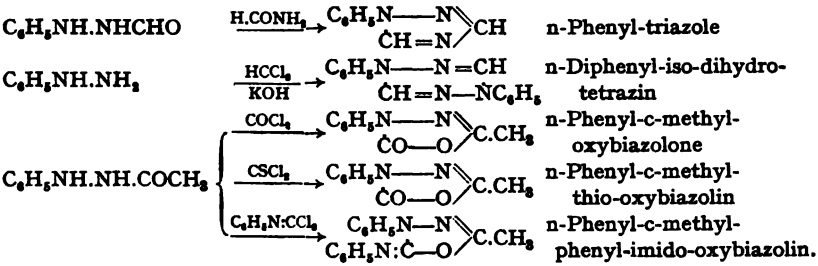
Sym. formyl-phenyl-hydrazide $C_6H_5NH.NH.CHO$, from formic acid and phenyl-hydrazin, melts at 145° (B. **27,** 1522; **28,** B. 764).

Unsym. or **α-aceto-phenyl-hydrazide** $C_6N_5N(COCH_3)NH_2$, m.p. 124°, is obtained from αβ-diaceto-phenyl-hydrazin, by heating with dilute sulphuric acid (B. **27,** 2964). **Sym.** or **β-aceto-phenyl-hydrazide** $C_6H_5NH.NHCOCH_3$, m.p. 128°, from phenyl-hydrazin with acetic anhydride, or by boiling with glacial acetic acid (A. **100,** 129). **αβ-Diaceto-phenyl-hydrazide** $C_6H_5N(CO.CH_3)NHCOCH_3$, m.p. 106°, from potassium phenyl in ether with acetyl chloride (B. **20,** 47). **Propionyl-iso-butyryl-phenyl-hydrazide,** m.p. 158° and 143°, see C. 1898, II. 1051.

Hetero-ring Formations of the Fatty Acid Phenyl-hydrazide Deri-

vatives.—*n-Phenyl-triazole* results when formyl-phenyl-hydrazide is heated with formamide (B. **27,** R. 801). *n-Diphenyl-iso-dihydro-tetrazin* is also a formic-acid derivative of phenyl-hydrazin. It results from the action of chloroform and caustic potash upon phenyl-hydrazin (compare action of chloroform and caustic potash upon primary amines : I. 236, and II. 84, isonitriles or carbylamines).

The sym. or β-acidyl-phenyl-hydrazides, treated with phosgene, thio-phosgene, and iso-cyan-phenyl chloride, yield heterocyclic compounds—the *oxybiazolin* derivatives (B. **26,** 2870), which can also be regarded as derivatives of carbonic acid :



Alcoholic Acid Derivatives of Phenyl-hydrazin. — Sym. **Phenyl-hydrazido-acetic acid** $C_6H_5NH.NH.CH_2CO_2H$, m.p. 158°, is obtained by reduction of glyoxylic phenyl-hydrazone, a process which can be reversed by oxidation with ammoniacal copper solution. Its ester is formed, besides the unsym. compound, from chloro-acetic *ester* and phenyl-hydrazin, whereas chloro-acetic *acid*, and its amides, yield unsym. **Phenyl-hydrazido-acetic acid** $C_6H_5N(NH_2)CH_2COOH$, m.p. 167°, or its derivatives (B. **36,** 3877 ; cp. also the behaviour of chloracetyl ureas and urethanes with phenyl-hydrazin (C. 1899, II. 421).

The ester of the unsym. acid is formed by reduction of nitroso-phenyl-glycin ester $C_6H_5N(NO)CH_2CO_2C_2H_5$ (B. **28,** 1223) ; amide, m.p. 150° ; anilide, m.p. 149°. Unsym. **Phenyl-hydrazide** $C_6H_5N(NH_2)CH_2CON(NH_2)C_6H_5$, m.p. 155° (A. **301,** 55) ; sym. **Phenyl-hydrazide** $C_6H_5N(NH_2)CH_2.CONHNHC_6H_5$, m.p. 178° (B. **29,** 622).

Unsym. **Phenyl-hydrazido-β-propionic ester** $C_6H_5N(NH_2).CH_2.CH_2.CO_2C_2H_5$, b.p. 175°, from nitroso-β-anilido-propionic ester (B. **29,** 515).

Unsym. **Phenyl-hydrazido-β-butyric acid** $C_6H_5N(NH_2).CH(CH_3)CH_2COOH$, m.p. 111°, from β-chloro-butyric acid with phenyl-hydrazin (*J. pr. Ch.* 2, **45,** 87).

Hetero-ring Formation of Phenyl-hydrazido-acids.—(1) With formamide, unsym. phenyl-hydrazido-acetic ester condenses to phenyl-keto-hydro-β-triazin.

(2) Similarly, unsym. anilido-acetic-α-phenyl-hydrazide $C_6H_5N(NH_2)CO.CH_2NHC_6H_5$, with cryst. formic acid, gives *n-diphenyl-keto-tetrahydro-α-triazin.*

(3) The 1-phenyl-semicarbazide-1-acetic ester $C_6H_5NH(CH_2COOR)NHCONH_2$, obtained from unsym. phenyl-hydrazido-acetic ester with potassium cyanate, on saponification, yields *n-phenyl-diketo-hexahydro-α-triazin.*

The phenyl-hydrazido-carboxylic acids 4, 5, and 6 (below), corre-

sponding to the β-oxy-acids, so easily develop anhydrides (**pyrazolidones** and **lactames**) that they frequently escape isolation.

1. $C_6H_5N.NH_2$ / $CH_2COOC_2H_5$ —HCONH$_2$→ $C_6H_5N{-}N{=}CH$ / $CH_2{-}CO{-}NH$ — n-Phenyl-keto-tetrahydro-*a*-triazin

2. $C_6H_5N.NH_2$ / $CO.CH_2.NHC_6H_5$ —HCOOH→ $C_6H_5.N{-}N{=}CH$ / $CO{-}CH_2{-}NC_6H_5$ — n-Diphenyl-keto-tetrahydro-*a*-triazin

3. $C_6H_5NH{-}NH{-}CO$ / $CH_2.CO_2RNH_2$ → $C_6H_5NH{-}NH{-}CO$ / $CH_2{-}CO{-}NH$ — n-Phenyl-diketo-hexahydro-*a*-triazin

4. $C_6H_5NHNH_2 + ClCH_2CH_2CO_2H \longrightarrow$ $C_6H_5.N{-}NH$ / $CH_2{-}CH_2$ > CO — 1-Phenyl-3-pyrazolidone

5. $C_6H_5NH.NH_2 + CH_3CH:CHCO_2H \rightarrow$ $C_6H_5N{-}NH$ / $CO{-}CH_2$ > $CH.CH_3$ — 1-Phenyl-3-methyl-5-pyrazolidone

6. $C_6H_5N{-}NH_2$ / $CH_3CH{-}CH_2{-}CO_2H$ → $C_6H_5N{-}NH_2$ / $CH_3CH{-}CH$ > CO — 1-Phenyl-5-methyl-3-pyrazolidone.

PHENYL-HYDRAZIN DERIVATIVES OF THE MONO-KETONIC ACIDS.—The α-, β-, and γ-ketone carboxylic esters react with phenyl-hydrazin, forming phenyl-hydrazones, just as the ketones do. The phenyl-hydrazones of α- and γ-ketone carboxylic acids are known. Zinc chloride or concentrated sulphuric acid rearranges the phenyl-hydrazones of the α-, β-, and γ-ketone carboxylic acids into indol derivatives (compare indol formation of the ketone phenyl-hydrazones). The phenyl-hydrazones of the β- and γ-ketone carboxylic esters and of the free γ-ketone carboxylic esters manifest great tendency to the lactazame formation. **Lævulinic phenyl-hydrazone** (1) yields *1-phenyl-3-methyl-pyridazinone* (*q.v.*), and under other conditions *α-methyl-indol-β-acetic acid.* **Aceto-acetic ester phenyl-hydrazone** $C_6H_5NH.N{=}C(CH_3).CH_2.CO_2C_2H_5$, melting at 50°, is formed on adding aceto-acetic ester to phenyl-hydrazin (B. **27**, R. 793), and spontaneously forms *1-phenyl-3-methyl-pyrazolone* (*q.v.*); whereas with acetyl chloride or excessive hydrochloric acid it yields *1-phenyl-3-methyl-5-ethoxy-pyrazole.*

HETERO-RING FORMATIONS OF THE PHENYL-HYDRAZONE KETONE ACIDS.

1. *Indol* condensation: p. 155.

$CH_3C{=}N{-}NHC_6H_5$ / $CH_2{-}CH_2{-}COOH$ → $CH_3C{-}NH$ / $COOH.CH_2.C{=}$ > C_6H_4 — *α*-Methyl-indol-*β*-acetic acid

2. *Lactazame:*

$C_6H_5.NH{-}N$ / $CO_2C_2H_5CH_2.C.CH_3$ → $C_6H_5N{-}N$ / $CO.CH_2.C.CH_3$ — 1-Phenyl-3-methyl-5-pyrazolone.

$C_6H_5.NH{-}N$ / $CO_2H.CH_2.CH_2.C.CH_3$ → $C_6H_5N{-}N$ / $CO.CH_2.CH_2C.CH_3$ — 1-Phenyl-3-methyl-pyridazinone

3. *Pyrazole:*

$C_6H_5.NH{-}N$ / $C_2H_5OCO.CH_2.C.CH_3$ → $C_6H_5N{-}N$ / $C_2H_5OC{=}CH.C.CH_3$ — 1-Phenyl-3-methyl-ethoxy-pyrazole.

PHENYL-HYDRAZIN DERIVATIVES OF CARBONIC ACID.—On saturating an aqueous solution of phenyl-hydrazin with CO_2 we obtain **Phenyl-hydrazin-phenyl-carbazinate** $C_6H_5NHNHCOONH_3NHC_6H_5$, a white

crystalline mass (A. **190,** 123; C. 1901, II. 1051). **Phenyl-carbazinic ethyl ester** $C_6H_5NHNHCOOC_2H_5$, m.p. 86°, is formed when $Cl.CO_2C_2H_5$ acts upon an etheric solution of phenyl-hydrazin. Heated to 240° it splits off alcohol, and passes into **Diphenyl-urazin** (A. **263,** 278; B. **26,** R. 20). Unsym. **Phenyl-hydrazido-formic ester** $C_6H_5N(NH_2)COOC_2H_5$, an oil, is formed from its aceto-compound obtained from aceto-phenyl-hydrazin, and chloro-formic ester (B. **29,** 829; **32,** 10). On further treatment with chloro-formic ester it gives **Phenyl-hydrazido-α,β-di-carboxylic ester** $C_6H_5N(CO_2C_2H_5)NH.CO_2C_2H_5$, m.p. 59°, with $COCl_2$; **Diphenyl-carbazide-dicarboxylic ester** $CO[NH.N(C_6H_5)CO_2C_2H_5]_2$, m.p. 159°. α- and β-**Cyano-phenyl-hydrazin** $C_6H_5(CN)N.NH_2$, two unstable oils, formed together by the action of cyanogen bromide upon phenyl-hydrazin (C. 1907, II. 802). On saponification, the α-compound yields α-**Phenyl-semicarbazide,** *carbaminic α-phenyl-hydrazide* $NH_2.N(C_6H_5).CO.NH_2$, m.p. 120°.

β-**Phenyl-semicarbazide,** *carbaminic β-phenyl-hydrazide* $C_6H_5NHNH CONH_2$, m.p. 172°, from phenyl-hydrazin salts, and potassium cyanate (A. **190,** 113), or by heating phenyl-hydrazin with urea or urethane. On heating, it passes into phenyl-urazol, and diphenyl-urazin, with formation of CO, CO_2, NH_3, and benzene (B. **21,** 1224). With potassium hypochlorite it forms diazo-benzolimide (B. **40,** 3033). Phenyl-semicarbazide changes into oxy-biazolone compounds with $COCl_2$, $CSCl_2$, and $C_6H_5NCCl_2$ (B. **26,** 2870), like sym. aceto-phenyl-hydrazin. For homologous aryl semicarbazides, see C. 1898, II. 199.

m-Tolyl-semicarbazide $CH_3C_6H_4NH.NH.CONH_2$, m.p. 184°, from m-tolyl-hydrazin and urea. It possesses antipyretic properties (C. 1905, I. 196; II. 1299).

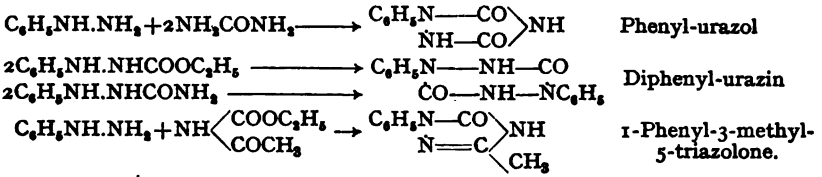
2, 4-Diphenyl-semicarbazide, *phenyl-carbaminic α-phenyl-hydrazide* $C_6H_5NH.CO.N(C_6H_5)NH_2$, m.p. 165°, is best obtained from phenyl-dithio-carbazinic ester $C_6H_5NHNHCSSCH_3$, by combining it with phenyl cyanate to $C_6H_5NHCON(C_6H_5).NHCSSCH_3$, converting the latter, with methyl iodide and alkali, into the dimethyl ester $C_6H_5 NHCON(C_6H_5)N : C(SCH_3)_2$ and then breaking up with dilute sulphuric acid. The 2, 4-diphenyl-semicarbazide is heated above its m.p. and converted into the isomeric **1, 4-Diphenyl-semicarbazide,** *phenyl-carbaminic β-phenyl-hydrazide* $C_6H_5NH.CO.NHNHC_6H_5$, m.p. 176°, which is distinguished from its isomers by its reaction with $FeCl_3$, and the resulting formation of an azo-body (B. **36,** 1362). **Triphenyl-semi-carbazide** $(C_6H_5)_2NCO.N(C_6H_5)NH_2$, m.p. 128°, formed as an aceto-compound, from diphenyl-urea chloride and β-aceto-phenyl-hydrazin (B. **33,** 246).

Diphenyl-carbazide, *phenyl-hydrazin-urea* $(C_6H_5NH.NH)_2CO$, m.p. 170°, obtained by heating urethane or phenyl carbonate with phenyl-hydrazin (B. **20,** 3372; C. 1900, I. 290); by boiling with alcoholic potash, or by the action of copper or mercury salts, it loses two H atoms and is transformed into salts of **Diphenyl-carbazone** $C_6H_5N : NCONHNHC_6H_5$, orange-red needles of m.p. 157° with decomposition (A. **263,** 274). With metals this diphenyl-carbazone forms red or blue and partly explosive salts of the type $C_6H_5N_2CONMeNHC_6H_5$, and it dyes silk or wool in a neutral bath. Like the diphenyl-carbazide, it is converted by oxidation, with silver and acetate, into **diphenyl-carbo-diazone** $(C_6H_5N : N)_2CO$, colourless needles, decomposing on heating, and re-

generating the K salt of diphenyl-carbazone on boiling with alcoholic potash (C. 1900, II. 1108; 1901, I. 703; II. 682).

Cyclic Urea and Carbamic Acid Derivatives.—*Phenyl-urazol* is produced on heating phenyl-semicarbazide, or phenyl-hydrazin chlorohydrate with urea, or biuret with phenyl-hydrazin. *Diphenyl-urazin* results upon heating ethyl-phenyl-carbazinate and phenyl-semicarbazide (A. **263**, 582).

1-*Phenyl*-3-*methyl*-5-*triazolone* is obtained from acetyl-urethane and phenyl-hydrazin (B. **22**, R. 737):



PHENYL-HYDRAZIN DERIVATIVES OF CARBONIC ACID.—On passing CS_2 through an etheric solution of phenyl-hydrazin we obtain **Phenyl-dithio-carbazimic phenyl-hydrazin** $C_6H_5NH.NH.CSSNH_3NHC_6H_5$, m.p. 96°. From solutions of the salts of **phenyl-dithio-carbazimic acid,** mineral acids precipitate the free acid in fine shiny flakes, easily oxidised to the corresponding bisulphide (A. **190**, 114). The mono- and dialkyl esters obtained from the acid with alkali and halogen alkyls are partly derivable from the desmotropic form of phenyl-sulpho-carbazinic acid $C_6H_5NHN : C(SH)_2$, corresponding to the formula

$$C_6H_5NHN : C(SCH_3)SH,\quad C_6H_5NHN : C(SCH_3)_2,\quad C_6H_5NHN : C\begin{cases}S—CH_2\\S—CH_2\end{cases}.$$

On introducing two different radicles, the resulting compounds $C_6H_5NHN : C\begin{cases}SR\\SR'\end{cases}$ occur in *stereo-isomeric* forms. Dilute acids break up the dialkyl esters of phenyl-dithio-carbazinic acid into phenyl-hydrazin and dithio-carbonic ester (see Vol. I. and B. **34**, 1119; *J. pr. Ch.* 2, **65**, 473). On treating the potassium salt of phenyl-sulpho-carbonic acid with $COCl_2$ or CS_2 we obtain **n-phenyl-thio-biazolone-sulphohydrate** and also the **dithio-sulphohydrate.**

α-Phenyl-sulpho-semicarbazide, *thio-carbaminic α-phenyl-hydrazide* $NH_2.N(C_6H_5)CS.NH_2$, m.p. 153°, from the action of NH_4SH upon α-cyano-phenyl-hydrazin.

β-Phenyl-sulpho-semicarbazide $C_6H_5NH.NH.CSNH_2$, m.p. 200°, isomeric with phenyl-thio-semicarbazide, is obtained from phenyl-hydrazin sulphocyanate at 160°–170°; on heating with HCl it passes into **sulpho-carbizin** and **benzo-diazo-thin** (B. **27**, 861).

2, 4-Diphenyl-sulpho-semicarbazide, *phenyl-thio-carbaminic α-phenyl-hydrazide* $C_6H_5NHCSN(C_6H_5)NH_2$, m.p. 139°, is obtained from phenyl-dithio-carbaminic acid with aniline, as well as the combination of phenyl-mustard oil with phenyl-hydrazin. It is transposed like the 2, 4-diphenyl-semicarbazide, but much more easily, into **2, 4-Diphenyl-sulpho-semicarbazide,** or *phenyl-thio-carbaminic β-phenyl-hydrazide* $C_6H_5NHCSNHNHC_6H_5$, m.p. 176°. Both isomeric compounds give, with methyl iodide and alkali, the isomeric methyl ethers $C_6H_5N : C(SCH_3)N(C_6H_5)NH_2$ and $C_6H_5N.C(SCH_3).NHNHC_6H_5$.

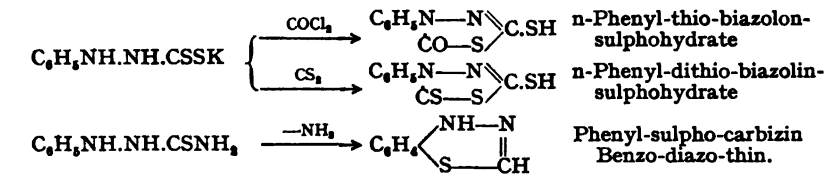
With benzaldehyde, the 2, 4-diphenyl-thio-semicarbazide reacts smoothly with formation of a benzylidene derivative, while the 1, 4-compound does not react in this manner. For other isomeric transpositions, see B. **34,** 320.

Diphenyl-sulpho-carbazide $(C_6H_5NH.NH)_2CS$, m.p. 150°, is formed by heating phenyl-hydrazin-phenyl-sulpho-carbazinate to 100°–110°.

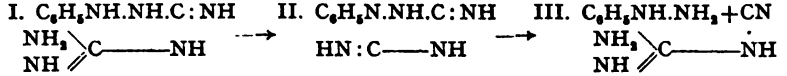
Diphenyl-sulpho-carbazone $C_6H_5N{=}N.CSNH.NHC_6H_5$, bluish-black crystals formed by short boiling of diphenyl-sulpho-carbazide with moderately concentrated alcoholic potash.

Diphenyl-sulpho-carbo-diazone $(C_6H_5N{=}N)_2CS$, from diphenyl-sulpho-carbazone by oxidation with manganese peroxide hydrate, forms small red needles (A. **212,** 316).

HETERO-RING FORMATION OF PHENYL-HYDRAZIN DI-THIO-CARBONIC ACID DERIVATIVES.



PHENYL-HYDRAZIN DERIVATIVES OF GUANIDIN.—**Anilino-guanidin** $NH : C(NH_2).NHNHC_6H_5$, and **Amido-phenyl-guanidin** $NH : C(NH_2).N(C_6H_5)NH_2$, are produced together from cyanamide and phenyl-hydrazin (B. **29,** R. 1109; cp. *J. pr. Ch.* 2, **61,** 440; C. 1901, II. 591); under different conditions a phenyl-hydrazin derivative of *biguanide* is formed, the unstable **Anilo-biguanide** $C_6H_5NH.NH.C : (NH).NH.C : (NH)NH_2$. On heating with cyanamide the anilo-biguanide (I.) passes into n-phenyl-guanazol (II.), which is also formed from diazano-diamide (III.) with phenyl-hydrazin (B. **24,** R. 649):



Dianilino-guanidin $NH : C(NH.NHC_6H_5)_2$, bromo-hydrate, m.p. 180°, is formed as a by-product in the action of BrCN upon phenyl-hydrazin.

PHENYL-HYDRAZIN DERIVATIVES OF DICARBOXYLIC ACIDS.—Corresponding to oxanilic acid and oxanilide we have **Oxal-phenyl-hydrazilic acid** $C_6H_5NH.NH.CO.CO_2H$, m.p. 110° (A. **236,** 197), and **Oxal-phenyl-hydrazide** $(C_6H_5NH.NH.CO)_2$, m.p. 278°.

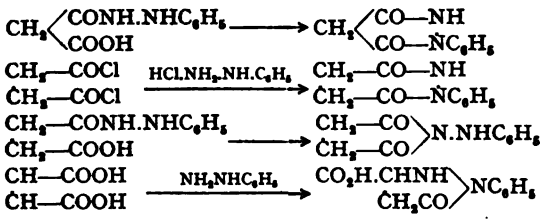
From *malonic acid* we have the following phenyl-hydrazin derivatives:—**Malonic ester phenyl-hydrazide,** *malono-phenyl-hydrazilic ester* $C_6H_5.NH.NH.CO.CH_2.COOC_2H_5$, m.p. 90°, from malonic ester chloride with phenyl-hydrazin. The compound easily dissolves in KHO, and, from the solution, HCl precipitates **Malonyl-phenyl-hydrazide,** or *1-phenyl-3, 5-pyrazolidone.* **Malonyl-diphenyl-hydrazide** $(C_6H_5NH.NH.CO)_2CH_2$, m.p. 187°, from malonic acid amide and phenyl-hydrazin at 200° (B. **25,** 1550).

Compounds of *ethylene-succinic acid* are known corresponding to

those of malonic acid :—**Succinic phenyl-hydrazilic ester,** m.p. 107° ; **Succinyl-phenyl-hydrazin** (see below), from phenyl-hydrazin chlorohydrate and succinyl chloride (B. **26,** 2181) ; **Succinyl-diphenyl-hydrazide,** m.p. 209° (B. **21,** 2462), and also **Anilo-succimide,** $(CH_2CO)_2NNHC_6H_5$.

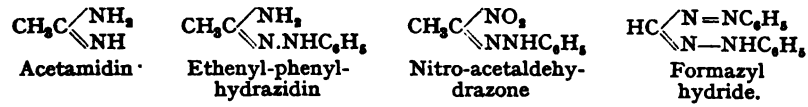
PHENYL-HYDRAZIN DERIVATIVES OF OLEFIN- AND OXY-DICARBOXYLIC ACIDS.—Maleïnic anhydride yields, with phenyl-hydrazin, **Maleino-phenyl-hydrazil.** On boiling maleïnic or fumaric acid in water with excess of phenyl-hydrazin, it adds itself as it does to acrylic or crotonic acid, and lactazame is formed subsequently (B. **26,** 117). **1-Phenyl-5-pyrazolidone-3-carboxylic acid** is formed.

HETERO-RING FORMATION OF PHENYL-HYDRAZIN DERIVATIVES OF DICARBOXYLIC ACIDS.



16. Hydrazidins or Amidrazones. Nitrazones. Phenyl-hydrazo-aldoximes. Phenyl-azo-aldoximes (Nitrosazones). Formazyl Compounds.

In connection with the phenyl-hydrazin derivatives of the carboxylic acids, some classes of compounds must be dealt with which are composed according to the amidine type. The hydrazidins are amidins in which the imido-group is replaced by the phenyl-hydrazone group. In the nitrazones there is also a replacement of the amido-group by the nitro-group, and, in the formazyl compounds, by the azo-phenyl group :



To these must be added the phenyl-azo-aldoximes, the stable transposition products of the very unstable nitroso-phenyl-hydrazones :

HYDRAZIDINS OR AMIDRAZONES.—**Ethenyl-phenyl-hydrazin** $CH_3C<^{N.NHC_6H_5}_{NH_2}$. The chlorohydrate of this base is formed by the action of phenyl-hydrazin upon hydrochloric acetimido-ether (B. **17,** 2002). **Cyan-amidrazone** or **dicyano-phenyl-hydrazin** $NC—C<^{N.NHC_6H_5}_{NH_2}$, m.p. 160°, with decomposition, and diamidrazone or cyano-phenyl-

hydrazin $\left(\begin{matrix}C_6H_5.NH.N\\ NH_2\end{matrix}\!\!>\!C\right)_2$, m.p. 225°, are formed by the action of cyanogen upon phenyl-hydrazin. Dicyano-phenyl-hydrazin is also formed by reduction of the prussic acid addition product of diazo-benzol cyanide, to which, therefore, probably the following formula must be ascribed: $C_6H_5N:NC\begin{matrix}NH\\ CN\end{matrix}$ (B. **28,** 2082; A. **287,** 300). The constitution of cyan-amidrazone follows from its formation by the action of phenyl-hydrazin upon **Flaveanic hydride** $NC—C\begin{matrix}S\\ NH_2\end{matrix}$, and the constitution of diamidrazone from its formation by the action of phenyl-hydrazin upon **Rubeanic hydride** $\begin{matrix}S\\ NH_2\end{matrix}\!\!>\!C—C\begin{matrix}S\\ NH_2\end{matrix}$ (see Vol. I.) and upon **Oxalo-diamido-oxime** $\begin{matrix}HON\\ NH_2\end{matrix}\!\!>\!C—C\begin{matrix}NOH\\ NH_2\end{matrix}$ (B. **26,** 2385). Diamidrazone is also formed by the reduction splitting of diformazyl.

Acetyl-amidrazone, *pyro-racemic acid phenyl-hydrazidine* $CH_3CO.C\begin{matrix}N.NHC_6H_5\\ NH_2\end{matrix}$, melting at 182°, is produced by reducing formazyl methyl-ketone with ammonium sulphide (B. **26,** 2783).

HETERO-RING FORMATIONS WITH THE AMIDRAZONES.—The amidrazones condense with carboxylic acids, their anhydrides or chlorides, to heterocyclic derivatives of the *triazol* group (*q.v.*). Nitrous acid converts the amidrazones into *tetrazol* derivatives (*q.v.*). Cyan-amidrazone is changed by acetic anhydride to n-phenyl-3-cyano-5-methyl-triazol; by nitrous acid to n-phenyl-3-cyan-tetrazol:

$$\begin{matrix}C_6H_5NH.N\\ NH_2\end{matrix}\!\!>\!C.CN \xrightarrow{CH_3COOH} \begin{matrix}C_6H_5N—N\\ CH_3C=N\end{matrix}\!\!>\!C.CN$$ n-Phenyl-3-cyan-5-methyl-triazol

$$\begin{matrix}C_6H_5NH.N\\ NH_2\end{matrix}\!\!>\!C.CN \xrightarrow{N_2O_3} \begin{matrix}C_6H_5N—N\\ N=N\end{matrix}\!\!>\!C.CN$$ n-Phenyl-3-cyan-tetrazol.

NITRO-HYDRAZONES or NITRAZONES are the nitro-compounds corresponding to the amidrazones; they are formed from the alkali salts of primary nitro-paraffins (Vol. I.) with diazonium salts, and were formerly regarded as nitro-azo-paraffins; but the free compounds must probably be regarded as nitrogenated hydrazones, while their metallic salts are derivable from the tautomeric form of **Phenyl-azo-nitro-acid** $RC\begin{matrix}NOOH\\ N:NC_6H_5\end{matrix}$. They are easily split up by alkalies into nitrites, and **β-Acidyl-phenyl-hydrazides** (B. **31,** 2626):

$$CH_3C(NO_2):NNHC_6H_5+KOH = CH_3CONHNHC_6H_5+NO_2K.$$

Certain poly-halogenated diazo-compounds also unite with primary nitro-paraffins in the molecular ratio 2 : 1, mixed azo-compounds being obtained (B. **36,** 3833).

Nitro-formaldehydrazone $CH(NO_2):N.NHC_6H_5$, occurs in two forms: α-form, m.p. 75°; β-form, m.p. 85° (B. **34,** 2002). With diazo-methane it yields an unstable O-methyl ether $HC(:NOOCH_3)N:NC_6H_5$, m.p. 54°, but with methyl iodide, and sodium methylate, it gives an N-methyl derivative $HC(NO_2):NN(CH_3)C_6H_5$, m.p. 92°, which, on reduction, yields **Phenyl-methyl-formhydrazin** $CH(NH_2):NN(CH_3)C_6H_5$, m.p. 101°, and then methyl-amine and unsym. phenyl-methyl-hydrazin (B. **34,** 574).

Nitro-acetaldehydrazone $CH_3C(NO_2):NNHC_6H_5$, yellow flakes, m.p. 142°, gives, with diazo-methane, O-methyl ether $CH_3C(:NOOCH_3).N:NC_6H_5$, m.p. 68°.

PHENYL-HYDRAZO-ALDOXIMES AND PHENYL-AZO-ALDOXIMES (NITROSAZONES).—**Formation** :—(1) On reducing nitrazones with Am_2S we obtain phenyl-hydrazo-aldoximes, which are easily oxidised, by ferric chloride, to phenyl-azo-aldoximes :

$$RC(NO_2):NNHC_6H_5 \xrightarrow{H} RC(:NOH)NHNHC_6H_5 \xrightarrow{O} RC(:NOH)N:NC_6H_5.$$

(2) The O-methyl ethers of the nitrazones, boiled in water, easily decompose into formaldehyde and phenyl-azo-aldoximes :

$$RC\begin{matrix}\diagup NOOCH_3 \\ \diagdown N:NC_6H_5\end{matrix} \longrightarrow RC\begin{matrix}\diagup NOH \\ \diagdown N:NC_6H_5\end{matrix} + CH_2O.$$

(3) Aldehyde-phenyl-hydrazones, treated with amyl nitrite and sodium alcoholate, or pyridin, probably first give the very unstable nitroso-hydrazones (nitrosazones), which easily transpose into azo-aldoximes (B. **35,** 54, 108 ; **36,** 53, 86, 347) :

$$RCH:NNHC_6H_5 \longrightarrow RC(NO):NNHC_6H_5 \longrightarrow RC(:NOH)N:NC_6H_5.$$

The aryl hydrazones of glyoxylic acid, treated with HNO_2, split off CO_2 and pass into phenyl-azo-aldoximes (C. 1905, I. 1538).

Phenyl-hydrazo-formaldoxime $HC(:NOH)NH.NHC_6H_5$, white needles, m.p. 113°, from nitro-formaldehydrazone, with alcoholic Am_2S, gives, by oxidation with ferric chloride, **Phenyl-azo-formaldoxime,** golden-yellow needles, m.p. 94° with decomposition.

Phenyl-hydrazo-acetaldoxime $CH_3C(:NOH)NHNHC_6H_5$, m.p. 128°, from nitro-acetaldehydrazone, gives by oxidation **Phenyl-azo-acetaldoxime** $CH_3C(:NOH)N:NC_6H_5$, m.p. 118°. This is obtained from the O-methyl ether of nitro-acetaldehydrazone on boiling with water, also from acetaldehyde-phenyl-hydrazone, or benzol-azo-ethane with amyl nitrite and sodium ethylate, or pyridin, and also from acetaldehyde-ammonia with nitroso-phenyl-hydrazin (B. **35,** 1009). Its Ag salt, with methyl iodide, gives the O-methyl ether $CH_3C(:NOCH_3)N:NC_6H_5$, an oil of $b.p._{12}$ 134° ; whereas the Na salt gives, with methyl iodide, an N-methyl ether, m.p. 96°. This latter, under the influence of sodium alcoholate, easily undergoes cyclic condensations into **Phenyl-methyl-triazol** :—

$$CH_3C\begin{matrix}\diagup O—NCH_3 \\ \diagdown N:NC_6H_5\end{matrix} \xrightarrow{-H_2O} CH_3C\begin{matrix}\diagup N=CH \\ \diagdown N—NC_6H_5\end{matrix}.$$

HCl converts the phenyl-azo-aldoximes, with primary addition, and wandering of the chlorine atom into the benzene nucleus, into **Chloro-phenyl-hydrazo-aldoximes** :

$$RC(:NOH)N:NC_6H_5 \xrightarrow{HCl} RC(:NOH)NH.NCl.C_6H_5 \longrightarrow RC(:NOH)NH.NHC_6H_4Cl.$$

FORMAZYL COMPOUNDS are strongly coloured, usually red, easily crystallised substances. Their sulpho-acids are dyes (B. **33,** 747). They are obtained (1) from phenyl-hydrazones and normal diazo-benzol, usually in alkaline solution ; (2) from phenyl-hydrazin and phenyl-hydrazides ; the hydrazone-hydrazide produced at first oxidises, under the influence of phenyl-hydrazin, with the loss of two hydrogen atoms ;

(3) from the phenyl-hydrazone chlorides, corresponding to the imide chlorides, by action of phenyl-hydrazin (B. **27,** 320 ; **29,** 1386).

Formazyl hydride $HC\langle^{N:NC_6H_5}_{N.NHC_6H_5}$, m.p. 116° (I. 233), has been obtained from formazyl-carboxylic acid by fusion, or by the action of diazo-benzol acetate upon malonic acid, or from acetyl-formazyl hydride $CH(N_2C_6H_5) : NN(COCH_3)C_6H_5$, generated on acetyling formazyl-carboxylic acid with methylated potash (*J. pr. Ch.* 2, **65,** 131).

Methyl-formazyl $CH_3C(N_2C_6H_5) : NNHC_6H_5$, m.p. 121°, see *J. pr. Ch.* 2, **64,** 213 ; B. **36,** 87.

Formazyl-methyl ketone $CH_3.CO.C\langle^{N:NC_6H_5}_{N.NHC_6H_5}$, m.p. 134°, results from the action of diazo-benzol upon acetone, aceto-acetic ester, pyro-racemic aldehyde hydrazone, and benzol-azo-acetyl acetone (B. **25,** 3211).

Formazyl-carboxylic acid $CO_2H.C\langle^{N:N_6H_5}_{N.NH.C_6H_5}$, m.p. 162° with decomposition, is made by saponifying the ethyl-formazyl-carboxylic ester, m.p. 117°. The latter is produced when diazo-benzol chloride acts upon aceto-acetic ester, oxalo-acetic ester (B. **25,** 3456), or upon phenyl-hydrazone-mesoxalic-ester acid. **Diformazyl** $\begin{matrix}C_6H_5N:N\\C_6H_5NH.N\end{matrix}\!\!>\!C.C\langle^{N:NC_6H_5}_{N.NHC_6H_5}$, greenish-brown, brilliant flakes, m.p. 226°. It results from the action of diazo-benzol chloride upon lævulinic acid, hydro-chelidonic acid, or acetone-diacetic acid, and from dioxy-tartrosazone.

Formazyl-acrylic acid $CO_2H.CH:CH.C\langle^{N:NC_6H_5}_{N:NHC_6H_5}$, m.p. 129° with decomposition, formed by the action of diazo-benzol acetate upon glutaconic acid (B. **40,** 4927).

Formazyl-azo-benzol, Phenyl-azo-formazyl $(C_6H_5N=N)_2C=N.NHC_6H_5$, m.p. 162°, from formazyl-carboxylic acid, glyoxalic phenyl hydrazone or acetaldehyde, with diazo-benzol in alkaline solution (*J. pr. Ch.* 2, **64,** 199). In the action of diazo-benzol alkali upon pyro-racemic acid, the first product is **Formazyl-glyoxalic acid,** m.p. 166°, which, on further action, is decomposed into oxalic acid and phenyl-azo-formazyl (*J. pr. Ch.* 2, **64,** 204).

Nitro-formazyl $NO_2.C(N_2C_6H_5) : NNHC_6H_5$, m.p. 153°, from sodium nitro-methane, with diazo-benzol nitrate, is both a formazyl and a nitrazone compound (B. **27,** 156 ; cp. B. **33,** 2043).

Hetero-ring Formations in Formazyl Compounds.—Under the influence of strong mineral acids the formazyl compounds split off aniline and give *pheno-triazin* derivatives : formazyl-carboxylic ester gives *a-pheno-triazin.* On oxidation, the formazyl compounds give tetrazolium compounds ; thus, from formazyl hydride **n-Diphenyl-tetrazolium hydroxide** is obtained :

$$\begin{matrix}C_6H_5N{=}N\\C_6H_5NH{-}N\end{matrix}\!\!>\!C.CO_2C_2H_5 \longrightarrow C_6H_4\langle^{N=N}_{N=CH} \qquad \textit{a}\text{-Pheno-triazin}$$

$$\begin{matrix}C_6H_5N{=}N\\C_6H_5NH{-}N\end{matrix}\!\!>\!CH \xrightarrow{O} \begin{matrix}C_6H_5N(OH):N\\C_6H_5N\text{———}N\end{matrix}\!\!>\!CH \qquad \text{n-Diphenyl-tetrazolium-hydroxide.}$$

Phenyl - nitroso - hydrazin $C_6H_5N\langle^{NO}_{NH_2}$ or $C_6H_5NHNHNO$, yellowish-brown crystalline flakes easily passing into diazo-benzol-imide (A. **190,**

89). Obtained from phenyl-hydrazin and HNO_2; an excess of acid oxidises phenyl-hydrazin to diazo-benzol nitrate (C. 1897, I. 381; B. **33,** 1718). Heating in indifferent solvents decomposes the phenyl-nitroso-hydrazin with nitrous oxide and aniline (B. **41,** 2809). By reduction it is split up with recovery of phenyl-hydrazin. A similar behaviour is shown by the nitroso-derivatives of alkylated phenyl-hydrazins.

Nitroso - α, β - diethyl - phenyl - hydrazin $C_6H_5N(C_2H_5)N(C_2H_5)NO$ yields ethyl-aniline and ethyl-hydrazin (B. **36,** 202). But in the reduction of **Nitroso-formyl-phenyl-hydrazin** $C_6H_5N(NO)NHCHO$, m.p. 85°, and **Nitroso-acetyl-phenyl-hydrazin** $C_6H_5N(NO)NHCOCH_3$, m.p. 63° with decomposition, with Na amalgam and alcohol, derivatives of an hypothetical phenyl-triazane $C_6H_5N(NH_2)_2$ are obtained, and these have been isolated in the form of their benzylidene compounds.

Benzylidene-formyl-phenyl-triazane $C_6H_5N(N:CHC_6H_5)NHCHO$, m.p. 183°, and **Benzylidene-acetyl-phenyl-triazane** $C_6H_5N(N:CHC_6H_5)NHCOCH_3$, m.p. 163° (B. **35,** 1900). **Nitroso-phenyl-semicarbazide** $C_6H_5N(NO)NHCONH_2$, m.p. 127° with decomposition, from phenyl-semicarbazide with NO_2Na and acetic acid, decomposes gradually even at ordinary temperatures, and more rapidly on heating, with formation of phenyl-azo-carbamide; boiling with potassium hydroxide yields diazo-benzol-imide (B. **28,** 1925).

Tetrazones, or *tetrazenes*, derived from the hypothetical nitrogen hydride $NH_2—N=N—NH_2$, are formed from the unsym. alkyl-phenyl- or diphenyl-hydrazins by oxidation with HgO in alcoholic or etheric solution, or with dilute ferric chloride solution:

$$2C_6H_5N(CH_3).NH_2+2O=C_6H_5.N(CH_3).N:N.N(CH_3).C_6H_5+2H_2O.$$

They are solid bodies, decomposed on melting or boiling with dilute acids. **Dimethyl-diphenyl-tetrazone** $C_6H_5.N(CH_3)N_2.N(CH_3)C_6H_5$, m.p. 133°. **Diethyl-diphenyl-tetrazone,** m.p. 108° (A. **252,** 281). **Tetra-phenyl-tetrazone** $(C_6H_5)_2N.N_2.N(C_6H_5)_2$, m.p. 123°, from **as-Diphenyl-hydrazin. p - Tetratolyl - tetrazone** $(CH_3C_6H_4)_2N.N_2.N(C_6H_4CH_3)_2$, fiery-yellow needles, m.p. 134° with decomposition, from unsym. p-ditolyl-hydrazin with MnO_4K in acetone solution. On heating in indifferent solvents the quaternary tetrazones decompose into nitrogen and tetra-aryl- hydrazin. In concentrated acids they dissolve with liberation of N, forming intensely blue solutions, the transformation products being the same as those obtained with the corresponding tetra-aryl-hydrazins (B. **41,** 3502).

Hydro-tetrazones, *tetrazanes*, derived from the hypothetical nitrogen hydride $NH_2.NH.NH.NH_2$, have been obtained by the oxidation of aldehyde-phenyl-hydrazones with HgO or amyl nitrite (B. **26,** R. 55; **27,** 2920). Thus, from benzal-phenyl-hydrazone the compound $\begin{matrix}C_6H_5.CH:N.NC_6H_5\\C_6H_5.CH:N.NC_6H_5\end{matrix}$ **Benzal-diphenyl-dihydro-tetrazone** is obtained, m.p. 190°. Under the influence of other oxidisers, *e.g.* aerial oxygen in alkaline solution, the aldehydrazones are oxidised to osazones of diketones. Thus, benzal-hydrazone is oxidised to benzile-osazone (A. **305,** 165). Concerning a third type of oxidation, producing the so-called *dehydro-benzal-phenyl-hydrazone* $\begin{matrix}C_6H_5C.N:NHC_6H_5\\C_6H_5N.N:CHC_6H_5\end{matrix}$, m.p. 207°, see C. 1897, II. 899; B. **34,** 528, etc.

18. **Buzylene or Diazo-hydrazo-compounds.**—In **Hippuryl-phenyl-buzylene** $C_6H_5N{=}N{-}NH{-}NHCO.CH_2NHCOC_6H_5$, m.p. 84°, we have a hippuric acid derivative of the unknown nitrogen hydride " buzylene " $NH{=}N{-}NH{-}NH_2$ (B. **26,** 1268). It is formed from hippuryl-hydrazin and diazo-benzol sulphate. From the same buzylene the **Diazo-benzol-phenyl-hydrazide** $C_6H_5N : N.N(C_6H_5).NH_2$, m.p. 71° with decomposition, is derived. It has been prepared (1) from diazo-benzol and phenyl-hydrazin; (2) from phenyl-hydrazin by oxidation with iodine solution (*J. pr. Ch.* 2, **66,** 336). By the first method a number of nucleus-substituted derivatives have also been prepared. As the unsym. hydrazins are converted into tetrazones, so these diazo-phenyl-hydrazides are converted, by oxidation with MnO_4K, into bodies containing a chain of eight N atoms.

19. **Octazones.—Bis-diazo-benzol-diphenyl-tetrazone,** *tetraphenyl-octazone* $C_6H_5N : N.N(C_6H_5)N : N.N(C_6H_5)N : NC_6H_5$, m.p. 51°; **bis-bromo-diazo-benzol-diphenyl-tetrazone,** m.p. 60°. These substances decompose, and explode very easily (B. **33,** 2741).

4. Aromatic Compounds of Phosphorus, Arsenic, Antimony, Bismuth, Boron, Silicon, and Tin.

The phenyl derivatives of phosphorus, arsenic, antimony, bismuth, boron, silicon, and tin are correlated to the aromatic nitrogen compounds. Their chlorides are most suitable for the preparation of these bodies. (1) They react with benzene at a red heat, hydrochloric acid being eliminated; (2) with benzene and aluminium chloride; (3) with mercury-diphenyl; (4) with phenyl-magnesium bromide (B. **37,** 4620); (5) with sodium and benzene chloride, or benzene bromide. This class of derivatives is produced also (6) from alloys of the elements with alkali metals and benzene haloids.

Special importance is attached, on account of their destructive action upon trypanosomes, to a series of aromatic compounds of arsenic which, being relatively but slightly poisonous, were found useful as medicines in protozoic diseases. It was found that compounds containing *trivalent* arsenic were much more effective than those containing quinquivalent arsenic (like those of cacodylic acid, Vol. I.). The monosodium salt of p-amido-phenyl-arsinic acid, known as "atoxyl," is used therapeutically for fighting " sleeping sickness " and the diamido-dioxy-arseno-benzol, in the form of its bichlorohydrate " salvarsan " (P. Ehrlich-Hata 666) for fighting syphilis.

PHENYL-PHOSPHORUS COMPOUNDS.—Michaelis in 1876 succeeded, by the preparation of phosphenyl chloride, the substance for obtaining phosphenyl derivatives, in overcoming the experimental difficulties which opposed the union of the phenyl residue with phosphorus (A. **181,** 265; **293,** 193, 325; **294,** 1). Some phosphenyl compounds in composition correspond to known aromatic nitrogen-containing substances; the names of the respective phosphenyl bodies recall these :

Aniline,	$C_6H_5NH_2$	$C_6H_5PH_2$,	Phenyl-phosphine
Nitro-benzol,	$C_6H_5NO_2$	$C_6H_5PO_2$,	Phosphino-benzol
Azo-benzol,	$C_6H_5N : NC_6H_5$	$C_6H_5P : PC_6H_5$,	Phospho-benzol.

Phenyl-phosphine $C_6H_5.PH_2$, *phosphaniline*, boiling at 160°, is obtained by the action of hydriodic acid and then alcohol upon phosphenyl chloride $C_6H_5.PCl_2$. It is a liquid possessing an extremely disagreeable odour. When exposed to the air, it oxidises to phosphenyl oxide $C_6H_5.PH_2O$, a crystalline mass easily soluble in water. Phenyl-phosphine combines with HI to the iodide $C_6H_5.PH_3I$, out of which water again separates phenyl-phosphine.

Phosphenyl chloride $C_6H_5.PCl_2$, boiling at 225°, with sp. gr. 1·319 (29°), is a strongly refracting liquid which fumes in the air. It is formed (1) by conducting a mixture of benzene and PCl_3 vapours through tubes heated to redness (A. **181**, 280); (2) by heating mercury-diphenyl with PCl_3; and (3) by the action of $AlCl_3$ upon benzene and PCl_3. Aided by this last reaction, the chloro-phosphine residue has also been introduced into *dimethyl-aniline* (B. **21**, 1497), and into *phenol-alkyl ether* (B. **27**, 2559). It forms the **tetrachloride** $C_6H_5.PCl_4$ with chlorine; this melts at 73°. With oxygen it yields the **oxychloride** $C_6H_5.PCl_2O$, boiling at 250°, and with sulphur *phosphenyl sulpho-chloride*, boiling at 205° (130 mm.). When the dichloride is heated with water, we obtain phenyl-hypophosphorous acid $C_6H_5.PHO.OH$, melting at 70°, while the tetrachloride forms phenyl-phosphinic acid $C_6H_5.PO.(OH)_2$, which melts at 150°.

p-Tolyl-phosphoro-chloride $CH_3[4]C_6H_4PCl_2$, forms a tetrachloride, which forms with aniline **tolyl-trianilido-phosphonium chloride** $CH_3[4]C_6H_4P(NHC_6H_5)_3Cl$, melting at 245°. Sodium hydroxide converts the latter into the **hydroxide** $CH_3C_6H_4P(NHC_6H_5)_3OH$, melting at 240° (B. **28**, 2214).

Phosphino-benzene $C_6H_5PO_2$, melting at 100°, is obtained from phosphenyl oxychloride and phenyl-hypophosphorous acid (B. **25**, 1747).

Phosphenyl chloride converts phenyl-phosphine into **phospho-benzol** $C_6H_5.P : P.C_6H_5$, melting at 150° (B. **10**, 812).

Diphenyl-phosphine chloride $(C_6H_5)_2PCl$, boiling at 320°, is obtained from phosphenyl chloride alone at 280°, or with mercury-diphenyl at 220° (B. **21**, 1505). With phenol it yields **phenoxyl-diphenyl-phosphine** $(C_6H_5)_2POC_6H_5$, boiling at 265°–270° (62 mm.) (B. **18**, 2118); and with dilute sodium hydroxide: **diphenyl-phosphine** $(C_6H_5)_2PH$, boiling at 280°, and **diphenyl-phosphinic acid** $(C_6H_5)_2PO.OH$, melting at 190° (B. **15**, 801).

Triphenyl-phosphine $(C_6H_5)_3P$, melting at 75° and boiling about 360°, is produced from $C_6H_5.PCl_2$, and bromo-benzol, or from PCl_3 and bromo-benzol by the action of sodium (B. **18**, R. 562). It combines with halogen alkyls to quaternary phosphonium salts; with α-halogen ketones, such as chloracetone CH_3COCH_2Cl, compounds are formed, which easily pass into so-called phospho-keto-betaïns $(C_6H_5)_3P\langle\begin{smallmatrix}CH_2\\O\end{smallmatrix}\rangle C\langle\begin{smallmatrix}OH\\CH_2\end{smallmatrix}$ (B. **32**, 1566). It forms, with bromine, the dibromide $(C_6H_5)_3PBr_2$, which is converted by water or alkalies into the dihydroxide $(C_6H_5)_3P(OH)_2$. At 100° this passes into the oxide $(C_6H_5)_3PO$. The latter melts at 143° and boils above 360°. It is also obtained from C_6H_5MgBr and $POCl_3$ (C. 1904, II. 1638). **Triphenyl-phosphine oxide** $(C_6H_5)_3PO$, is isomeric with *phenoxyl-diphenyl-phosphine* $(C_6H_5)_2POC_6H_5$. Both compounds, in vapour density determinations made with reduced pressure, yield values according with the simple molecular formulas. Phosphorus, therefore, in the first body

is quinquivalent, and in the second it is trivalent (Michaelis and La Coste, B. **18,** 2118).

PHENYL-ARSENIC COMPOUNDS.—Reactions, similar to those used in obtaining the phenyl substitution products of phosphorus chloride, have been used with arsenic, and the following bodies have been obtained :—**Phenyl-arsenious chloride** $C_6H_6AsCl_2$; **Diphenyl-arsenious chloride** $(C_6H_5)_2AsCl$; **Triphenyl-arsin** $(C_6H_5)_3As$; **Phenyl-arsinic acid** $C_6H_5AsO(OH)_2$; **Diphenyl-arsinic acid** $(C_6H_5)_2AsOOH$.

Arseno-benzol $C_6H_5As : AsC_6H_5$ (A. **201,** 191 ; **207,** 195 ; **270,** 139 ; **321,** 141 ; B. **19,** 1031 ; **25,** 1521 ; **27,** 263). **p-Amido-phenyl-arsinic acid,** *arsanilic acid* $NH_2C_6H_4AsO(OH)_2$, brilliant white needles, m.p. above 200°, is formed besides **p_2-diamido-diphenyl-arsinic acid** $(NH_2C_6H_4)_2AsOOH$, m.p. 232°, by heating aniline arsenate to 190°–200° (B. **41,** 2367). By reduction with HI and SO_2 the amido-phenyl-arsinic acid passes into **p-amido-phenyl-arsinic oxide** $NH_2C_6H_4AsO.2H_2O$, whereas with tin, and HCl, it passes into the yellow p_2-diamido-arseno-benzol $NH_2C_6H_4As : AsC_6H_4NH_2$, m.p. 140° (C. 1909, I. 963).

From arsanilic acid, through the diazo-compound, **p-oxyphenyl-arsinic acid** $HOC_6H_4As(OH)_2$, m.p. 174° is formed. This can also be obtained direct by heating phenol with arsenic acid (C. 1909, I, 807). On nitrifying and reducing this to **m-amido-p-oxy-phenyl-arsinic acid** $HO(NH_2)C_6H_3AsO(OH_2)$, the **m, m-diamido-p, p-dioxy-arseno-benzol** $HO(NH_2)C_6H_3As : AsC_6H_3(NH_2)OH$ is obtained, the dichlorohydrate of which is the before-mentioned *salvarsan.* For homologous amido-phenyl-arsinic acids and their transformation products, see B. **41,** 3859.

Triphenyl-stibin $(C_6H_5)_3Sb$, m.p. 48°, is produced on introducing sodium into a solution of chloro-benzol and of antimonious chloride in benzene (A. 233, 43). Also from C_6H_5MgBr and $SbCl_2$ (B. **37,** 4621). On heating with antimonious chloride in xylol, it yields **phenyl-stibinous chloride,** m.p. 58°, b.p. 290°, starting from which, the **oxide, sulphide, tetrachloride,** and **phenyl-stibinic acid** have been prepared (B. **31,** 2910). **Triphenyl-stibin sulphide** $(C_6H_5)_3SbS$, m.p. 120°, from triphenyl-stibin bromide with Am_2S (B. **41,** 2762).

Bismuth-triphenyl $(C_6H_5)_3Bi$, m.p. 78°, is prepared by heating bromo-benzol and bismuth sodium (A. **251,** 324). **Diphenyl-bismuth iodide** $(C_6H_5)_2BI$, m.p. 133° (B. **30,** 2843).

PHENYL-BORON COMPOUNDS.—**Phenyl-boron chloride** $C_6H_5BCl_2$, m.p. 0°, and b.p. 175°, and **diphenyl-boron chloride** $(C_6H_5)_2BCl$, b.p. 271°, result from the interaction of mercury-diphenyl and boron chloride. **Phenyl-boron bromide** C_6H_5BBr, m.p. 330°, b.p.$_{20}$ 100°. **Diphenyl-boron bromide** $(C_6H_5)_2BBr$, m.p. 25° (B. **27,** 244 ; A. **315,** 29).

PHENYL-SILICON COMPOUNDS. — **Phenyl-silico-chloride** $C_6H_5.SiCl_3$ is prepared by heating mercury-diphenyl and $SiCl_4$ to 300°. It boils at 197° (Ladenburg, A. **173,** 151). Water decomposes it into **silico-benzoic acid** $C_6H_5.SiO.OH$, m.p. 92°. Alcohol forms **ortho-silico-benzoic acid ester** $C_6H_5.Si(O.C_2H_5)_3$, b.p. 137°. Zinc ethyl converts the chloride into **triethyl-phenyl silicide** $C_6H_5.Si.(C_2H_5)_3$, b.p. 230°. **Triphenyl-methyl silicide** $(C_6H_5)_3SiCH_3$, m.p. 67°, and **triphenyl-ethyl silicide** $(C_6H_5)_3SiC_2H_5$, m.p. 76°, are obtained from **triphenyl-silico-chloride** $(C_6H_5)_3SiCl$ with methyl- and ethyl-magnesium iodide respectively (C. 1908, I. 1266). Mixed alkyl-silicon compounds with four different radicles, like **phenyl-methyl-ethyl-propyl-silicon** $C_6H_5SiCH_3$

$(C_2H_5)(C_3H_7)$, a liquid of b.p: 231°, are formed by treating silicon chloride successively with phenyl, methyl, ethyl, and propyl magnesium bromides (C. 1907, I. 1192). Concerning optically active silicon compounds, see C. 1908, I. 1688; 1909, I. 360; 1910, I. 2083.

Triphenyl-silicane $(C_6H_5)_3SiH$, m.p. 203° (B. **40,** 2278).

Tetraphenyl-silicon $Si(C_6H_5)$ is produced by the action of sodium upon a mixture of $SiCl_4$, chloro-benzol, and ether (B. **19,** 1012). It melts at 228° and boils above 300°. On heating with bromine it yields triphenyl-silicon bromide $(C_6H_5)_3SiBr$, m.p. 120°, which on boiling with potash solution becomes triphenyl-silicol $(C_6H_5)_3SiOH$, m.p. 155° (C. 1899, II. 57; 1901, I. 999; B. **40,** 2275). **Diphenyl-silicol** $(C_6H_5)_2Si(OH)_2$, m.p. 139°, on melting, passes into **trimolecular diphenyl-silicon** $[(C_6H_5)_2SiO]_3$, m.p. 110° (C. 1904, I. 1257).

PHENYL-TIN COMPOUNDS.—Mercury diphenyl and stannic chloride interact to form **tin-diphenyl chloride** $(C_6H_5)_2SnCl_2$, m.p. 42° (A. **194,** 145; **282,** 328).

Tin-tetraphenyl $Sn(C_6H_5)_4$ is produced by the action of tin-sodium upon bromo-benzol, m.p. 226° and b.p. above 420° (B. **22,** 2917). Also by the action of tin tetrachloride upon phenyl-magnesium bromide.

5. Phenyl Metal Derivatives.

The phenyl group has been combined with magnesium, mercury, and lead.

Magnesium-diphenyl $(C_6H_5)_2Mg$, is a light, yellowish-white powder, dissolving readily in a mixture of benzene and ether. It is produced on heating mercury-diphenyl with magnesium powder and some acetic ester to 180°–185° (A. **282,** 320). In air it undergoes spontaneous combustion; water decomposes it violently with formation of $Mg(OH)_2$ and benzene.

ARYL-MAGNESIUM HALOIDS.—**Phenyl-magnesium bromide** C_6H_5MgBr, and **phenyl-magnesium iodide** C_6H_5MgI, as well as homologous aryl-magnesium haloids, are formed in a manner analogous to the alkyl-magnesium haloids, by the action of magnesium upon the etheric solutions of bromine and iodine benzols. They are as suitable for synthetic reactions as are the alkyl-magnesium haloids:

(1) With CO_2 they unite to form salts of aromatic carboxylic acids, *e.g.* C_6H_5COOH. (2) With COS they form thiol-carboxylic acids C_6H_5COSH, besides triphenyl-carbinols $(C_6H_5)_3COH$. (3) With CS_2, carbo-thio-acids are formed, *e.g.* C_6H_5CSSH. (4) Triphenyl-carbinol is formed from C_6H_5MgBr with phosgene and benzoic ester. (5) With mustard oils, thio-anilides are formed, $CH_3CSNHC_6H_5$. (6) With iso-nitriles, alkylated aldehydimines $C_6H_5CH{=}NCH_3$. (7) With diazo-benzol-imide $C_6H_5N_3$, diazo-amido-benzol $C_6H_5N_2NHC_6H_5$. (8) The action of nitroxyl chloride upon phenyl-magnesium bromide produces nitroso-benzol. (9) With S and Se, thio-phenols and seleno-phenols are formed, C_6H_5SH, and C_6H_5SeH. (10) With iodine, iodo-benzol and MgBrI, etc. (C. 1901, I. 1357; 1903, I. 568, 1403; 1909, II. 1349; B. **35,** 2692; **36,** 587, 910, 1007, 1588, 2116; **37,** 875; **39,** 3219).

Mercury-diphenyl $(C_6H_5)_2Hg$, m.p. 120°, is formed by treating bromo-benzol in benzene solution for some time with liquid sodium amalgam (Otto and Dreher, A. **154,** 93); the addition of some acetic

ether facilitates the reaction. It is also obtained by the action of $HgCl_2$ or HgCl upon phenyl-magnesium bromide (B. **37,** 1127). It crystallises in colourless, rhombic prisms, and can be sublimed. It assumes a yellow colour in sunlight. It dissolves readily in benzene and carbon disulphide, but with more difficulty in ether and alcohol; in water it is insoluble. When distilled, it decomposes for the most part into diphenyl, benzene, and mercury. The action of sodium upon mercury-diphenyl in benzene solution, produces sodium amalgam and **sodium-phenyl** C_6H_5Na, a body capable of many reactions (C. 1903, II. 195). Acids decompose it, with formation of benzene and mercury salts. Haloid compounds are produced by the action of the halogens—*e.g.* **mercury-phenyl chloride** C_6H_5HgCl, m.p. 250°; **mercury-phenyl bromide** C_6H_5HgBr, m.p. 275°; **mercury-phenyl iodide** C_6H_5HgI, m.p. 265°. **Mercury-phenyl hydroxide** C_6H_5HgOH is produced when silver oxide and alcohol act upon the chloride (*J. pr. Ch.* I. 186).

Mercury-phenyl acetate $C_6H_5Hg.O.COCH_3$ is also formed direct by heating benzene with mercury acetate to 110°–120°. Similarly, the mercury atom is easily introduced in the place of the nuclear H atom in other aromatic compounds, such as nitro-benzols, anilines, phenols, benzoic acid, etc., so that we may speak, not only of chlorination, nitrogenation, and sulphuration, but also of a "mercuration" of aromatic substances, as a general reaction. In these combinations the mercury is rather firmly attached to the nucleus. When the action is strong, several H atoms are replaced, and we may obtain compounds like $C_6H_4(Hg.OCOCH_3)_2$, $C_6H_3(HgO.COCH_3)_3$, and $C_6H_2(HgO.COCH_3)_4$ (B. **35,** 2032, 2853; C. 1899, I. 734; 1900, I. 1097).

Mercury-dialphyls. See A. **173,** 162; B. **14,** 2112; **17,** 2374; **20,** 1719; **22,** 1220, etc.

Lead-tetraphenyl $(C_6H_5)_4Pb$ is formed by heating bromo-benzol with lead-sodium and acetic ester. It melts at 224° (B. **20,** 3331). Also from lead chloride, and phenyl-magnesium bromide (B. **37,** 1126).

6. Sulphonic Acids.

The ease with which sulphonic or sulpho-acids are produced distinguishes the aromatic hydrocarbons from the aliphatic compounds in the same manner as does the easy formation of nitro-compounds. The introduction of sulpho-groups, in the place of aromatic H atoms, is called "*sulphonation.*"

Formation.—(1) The sulpho-acids of benzene hydrocarbons, and other benzene derivatives, are easily produced by mixing or heating them with concentrated or fuming sulphuric acid. In this manner it is possible to combine three sulpho-groups with one benzene nucleus:

$$C_6H_6+HO.SO_3H = C_6H_5.SO_3H+H_2O.$$

(2) In the action of an excess of chloro-sulphonic acid $Cl.SO_2OH$ the principal products, with careful cooling, are the chlorides of the sulpho-acids (B. **12,** 1848; **28,** 2172). The reaction then proceeds in the following way (B. **22,** R. 739):

$$C_6H_6+ClSO_2OH = HCl + C_6H_5.SO_2OH$$
$$C_6H_5SO_2OH+ClSO_2OH = H_2SO_4+C_6H_5SO_2Cl.$$

Sulphones are secondary products (p. 182).

(3) Further, sulphonic acids can be obtained from the diazo-amido-derivatives by boiling with sulphurous acid.

(4) By the oxidation of thio-phenols. This reaction proves that the sulphur atom of the sulpho-group is in union with the aromatic nucleus (compare mercaptans).

(5) By the oxidation of sulphinic acids.

Properties and Transformations.—Many aromatic sulpho-acids are very soluble in water and crystallise with difficulty. They can be separated from aqueous solution in the form of their sodium salts by means of sodium chloride : *salting out* (B. **28,** 91). In a cathode-ray vacuum many sulpho-acids can be distilled without decomposition (B. **33,** 3207). The ready solubility of the sulpho-acids, in conjunction with their easy production, meets with an important technical application in the conversion of aromatic dyes insoluble in water into their sulpho-acids, which dissolve in water with ease.

(1) The chlorides of the acids are made by acting upon the alkali salts with $POCl_3$ and PCl_5, and from the acids themselves by the action of PCl_5. The chlorides are converted into amides, esters, etc., as indicated under the alkyl-sulphonic acids (Vol. I.). The esters of the sulpho-acids are transposed by alcohol at 140°–150°, with the production of ethers (Vol. I.). Heating with phenols and with amines also makes the benzol-sulphonic esters transfer their alkyl groups to the former, so that they are generally useful as means of alkylation (A. **327,** 120). The sulphonamides are stable and crystallise well ; they are frequently prepared for the characterisation of a sulpho-acid.

(2) Hydrocarbons (together with phenyl sulphones) are formed when the free acids are subjected to distillation :

$$C_6H_5.SO_3H = C_6H_6+SO_3.$$

This rupture is more easily accomplished by heating the acids with concentrated HCl to 150°, or by distilling the ammonium salt of the sulphonic acid, or a mixture of the lead salt with ammonium chloride (B. **16,** 1468). The decomposition results with least difficulty by conducting steam into the dry sulpho-acid, or its solution in concentrated sulphuric acid ; superheated steam is most effective (B. **19,** 92).

(3) The SO_2Cl group in the sulpho-chlorides can be replaced by chlorine through the action of PCl_5. In some sulphonic acids free chlorine and bromine are capable of eliminating the sulpho-group and introducing the halogens (B. **16,** 617).

(4) The sulpho-group in many sulphonic acids is often replaced by NO_2 upon treating them with concentrated nitric acid.

(5) The sulphonic acids of the alkyl-benzols, more frequently applied in the form of their sulphamides, yield sulpho-carboxylic acids upon oxidation. The oxidation of o-toluol-sulphamide to the sulphimide of o-sulpho-benzoic acid (*q.v.*), called *saccharin,* is technically important.

(6) The chlorides of the aromatic sulpho-acids become thio-phenols upon reduction (cp. C. 1900, I. 252 ; 107, II. 397) :

$$C_6H_5SO_2Cl+6H = C_6H_5SH+2H_2O+HCl.$$

This reaction, like that of the oxidation of thio-phenols to sulphonic

acids, demonstrates that in the sulpho-acids the sulphur is in immediate union with the benzene nucleus.

(7) The sulphonic acids are not decomposed upon boiling them with aqueous alkalies. Phenols are formed when they are fused with alkalies. This reaction serves for the technical preparation of resorcin and other phenols :

$$C_6H_5.SO_3K+KOH = C_6H_5.OH+SO_3K_2.$$

(8) When distilled with potassium cyanide (or dry yellow prussiate of potash) nitriles result :

$$C_6H_5.SO_3K+CNK = C_6H_5.CN+SO_3K_2,$$

and these may be readily saponified to carboxylic acids.

(9) Carboxylates are also obtained on fusing the alkali sulphonates with sodium formate.

(10) Melting sulpho-acids with Na amide yields anilines (B. **19,** 903 ; **89,** 3014) :

$$C_6H_5SO_3Na+NaNH_2 = C_6H_5NH_2+SO_3Na_2.$$

MONOSULPHONIC ACIDS.—**Benzol-sulphonic acid** $C_6H_5.SO_3H$, m.p. 66°, b.p. 135°–137°, crystallises from water, in which it is exceedingly soluble, in plates containing water of crystallisation.

The **barium salt** $(C_6H_5.SO_3)_2Ba+H_2O$ forms pearly flakes, and is sparingly soluble in alcohol.

The **chloride** $C_6H_5.SO_2Cl$, m.p. 14·5°, b.p. 116° (B. **25,** 2257 ; C. 1900, I. 252), has a specific gravity of 1·378 at 23°. It slowly reverts to the acid upon boiling with water.

Methyl ester, b.p.$_{20}$ 154° (C. 1903, I. 396).

The **ethyl ester,** b.p.$_{15}$ 156°, obtained by the action of ethyl alcohol on the chloride, is decomposed into benzol-sulphonic acid and ethyl ether (Vol. I.) when it is heated to 150° with ethyl alcohol.

Benzol-sulphamide $C_6H_5.SO_2.NH_2$, m.p. 150°.

Benzol-sulphone-anilide $C_6H_5SO_2NHC_6H_5$, m.p. 110°. The benzol-sulphamides of the primary bases are mostly soluble in alkali ; their behaviour towards benzol sulpho-chloride may therefore be used for determining whether an amine base is primary or secondary (cp. B. **33,** 477 ; **38,** 906). Concentrated sulphuric acid splits up the benzol-sulphonamides into their components (A. **867,** 157).

Dibenzol-sulphimide $(C_6H_5SO_2)_2NH$, from sodium-benzol-sulphimide with benzol sulpho-chloride (C. 1901, II. 1185). **Benzol-sulpho-dichlor-amide** $C_6H_5SO_2NCl_2$, m.p. 76°, is formed by the action of sodium hypo-chlorite upon benzol-sulphamide. The latter is regenerated by HCl and HI, with liberation of chlorine and iodine. With alkalies in the cold, salts of benzol-sulpho-monochloramide are formed in which the alkali is probably linked to oxygen : $C_6H_5SO(OK) : NCl$ (C. 1905, I. 1010).

Benzol-sulpho-nitramide $C_6H_5SO_2NHNO_2$ consists of colourless plates, readily soluble in water. It decomposes at 100° into benzol-sulphonic acid and nitrous oxide. It is formed when a mixture of nitric and sulphuric acids acts upon benzol-sulphamide. Its **potassium salt** $C_6H_5SO_2NK.NO_2$, m.p. 275°, when reduced by glacial acetic acid and zinc dust becomes **benzol-sulphono-hydrazide** $C_6H_5SO_2NH.NH_2$,

m.p. 105° with decomposition, which also form benzol sulpho-chloride with hydrazin hydrate.

Benzol-sulphone-phenyl-hydrazide, phenyl-benzol-sulphazide (see above). **Dibenzol-sulphone-hydrazin** $(C_6H_5SO_2.NH)_2$, m.p. 228°. **Benzol-sulphone-azode** $C_6H_5SO_2.N_3$, an oil, is, in contrast with carboxylic azides, not attacked by hot water or alcohol (*J. pr. Ch.* 2, **58**, 160).

The sulphamide and nitrous acid yield **dibenzol-sulphon-hydroxylamine** $(C_6H_5SO_2)_2NOH$, which can also be made by the interaction of benzol-sulphinic acid and sodium nitrite; with diazo-benzol chloride the product is **benzol-sulpho-diazo-benzol-amide** $C_6H_5SO_2NH—N=N.C_6H_5$, m.p. 101° (B. **27**, 598).

Benzo-sulpho-hydroxamic acid $C_6H_5SO_2.NHOH$, m.p. 126°, is obtained from benzol-sulpho-chloride and hydroxylamine. Alkalies decompose it into benzol-sulphinic acid and hyponitrous acid (B. **29**, 1559, 2324):

$$2C_6H_5SO_2NHOH+4KOH = 2C_6H_5SO_2K+(NOK)_2+4H_2O.$$

With aldehydes, benzo-sulpho-hydroxamic acid passes into benzol-sulphinic acid and carbo-hydroxamic acids (C. 1901, II. 99).

Benzol-sulpho-isocyanate $C_6H_5SO_2NCO$, b.p.$_9$ 130°, from benzol-sulpho-chloride and silver cyanate. An oil of feeble odour, exhibiting all the properties and transformations of the isocyanates (B. **87**, 690).

TOLUOL-SULPHONIC ACIDS.—In sulphonating, toluol-o- and p-acids are the chief products. The o-acid can be obtained from p-tolyl-hydrazin-o-sulphonic acid free from the p-acid. The m-acid is obtained from p-toluidin-m-sulphonic acid. **o-Toluol-sulpho-chloride** is a liquid, formed from o-toluol-sulphinic acid and Cl (C. 1901, II. 961; B. **38**, 730). **o-Toluol-sulphamide** melts at 155° (see o-Sulpho-benzoic acid). **m-Toluol-sulphonic acid** $CH_3[1]C_6H_4[3]SO_3H+H_2O$; its chloride is a liquid; its amide melts at 107°. **p-Toluol-sulphonic acid** $CH_3[1]C_6H_4[4]SO_3H+4H_2O$; melts at 35°, b.p. 147°; its chloride melts at 69°, and boils at 145° (15 mm.); its bromide melts at 96°, its iodide at 84°, and its amide at 137°. Methyl ester, m.p. 28°; ethyl ester, m.p. 33° (A. **327**, 121).

Ditoluol-sulpho-hydroxamic acid $(C_7H_7.SO_2)_2NOH$ melts with decomposition at 148°. It results from the action of sodium nitrite upon toluol-sulphinic acid. It combines with an additional molecule of the sulphinic acid to **tritoluol-sulphonamide** $(C_7H_7.SO_2)_3N$, melting at 190° (*J. pr. Ch.* 2. **54**, 95; C. 1901, I. 455). Further derivatives of p-toluol-sulphonic acid, see B. **34**, 2996.

XYLOL-SULPHONIC ACIDS.—**1, 2-Xylol-4-sulphonic acid**: its *chloride* melts at 51°, its *amide* at 144°. **1, 3-Xylol-4-sulphonic acid**: its *chloride* melts at 34°, and its *amide* at 137°. **1, 3-Xylol-2-sulphonic acid**: its *amide* melts at 95°. **1, 4-Xylol-3-sulphonic acid**: its *chloride* melts at 25°, and its *amide* at 247°. They result upon sulphonating the various xylols.

[1, 2, 4]-Pseudo-cumol-5-sulphonic acid $(CH_3)_3C_6H_2SO_3H+2H_2O$ melts at 111°. Its *chloride* melts at 61°, and the *amide* at 181°. **Mesitylene-sulphonic acid** $C_9H_{12}SO_3+2H_2O$ melts at 77°, its *chloride* at 57°, and its *amide* at 141°.

POLY-SULPHONIC ACIDS.—**Benzol-disulphonic acids** $C_6H_4\langle^{SO_3H}_{SO_3H}$. On heating benzene with fuming sulphuric acid to 200° C., we get *meta*- and *para*-benzol-disulphonic acids, with the former in predominating quantity, but by prolonged heating it passes into the *para*-variety (B. **9**, 550). *Meta*-disulphonic acid is produced from disulphanilic acid by means of the diazo-compound.

Ortho-benzol-disulphonic acid is formed from meta-amido-benzol-sulphonic acid by further introduction of the sulpho-group, and replacement of NH_2 by hydrogen. The melting-points of the sulpho-chlorides and sulphamides of the three isomeric disulphonic acids are :

	Ortho.	Meta.	Para.
$C_6H_4(SO_2Cl)_2$	105°	63°	132°
$C_6H_4(SO_2NH_2)_2$	233°	228°	288°.

The corresponding *dicyanides*, $C_6H_4(CN)_2$, the nitriles of the three phthalic acids, are obtained by distillation with potassium cyanide or potassium ferrocyanide. When fused with potassium hydroxide, both *meta* and *para* acids yield resorcin (meta-dioxy-benzol) ; at lower temperatures meta-phenol-sulphonic acid $C_6H_4(OH)SO_3H$ results at first from both acids.

Benzol-trisulphonic acid $C_6H_3(SO_3H)_3$ (1, 3, 6) is easily made by heating potassium m-benzol disulphonate with common sulphuric acid (B. **21**, R. 49). The free acid (from the lead salt) crystallises in long needles with $3H_2O$; its *chloride* melts at 184°, its *amide* at 306°. Fused with caustic potash, it yields *phloroglucin* $C_6H_3(OH)_3$, or 1, 3, 5-trioxy-benzol; and upon heating with potassium cyanide it forms the trinitrile, which upon saponification becomes *trimesinic acid* $C_6H_3(CO_2H)_3$.

Toluol-disulphonic acids. The six possible isomerides are known (B. **20**, 350 ; **29**, R. 868).

Xylol-disulphonic acids (B. **25**, R. 700).

Benzol-seleno-acid $C_6H_5SeO_2OH$, hygroscopic needles, m.p. 142°, is formed by heating benzene with selenic acid to 100°–110°, as well as by oxidation of phenyl-diselenide with chlorine water. It detonates on heating to 180°, yielding oxygen, phenyl-selenide, and phenyl-diselenide. Reduction with SH_2 or SO_2 converts it into seleno-phenol. With concentrated HCl it develops Cl, even in the cold, being reduced to benzol-seleninic acid (C. 1909, II. 20).

CHLORO-, BROMO-, IODO-, IODOSO-, NITRO-, NITROSO- and AMIDO-BENZOL-SULPHONIC ACIDS.—The chloro-, bromo- and iodo-benzol-sulphonic acids are prepared from the three amido-benzol-sulphonic acids by means of the diazo-reactions (B. **28**, 90). p-Compounds are the principal products in the sulphonation of chloro- and bromo-benzols. In nitrating benzol-sulphonic acid and sulphonating nitro-benzol the three isomeric nitro-benzol-sulphonic acids are produced with the m-derivatives in predominating quantity (A. **177**, 60).

o- and p-Nitro-benzol-sulphonic acids are best prepared by oxidation of the corresponding nitro-benzol-disulphides $(NO_2C_6H_4S)_2$, obtained from the nitro-chloro-benzols, with fuming sulphuric acid (B. **35**, 651 ; C. 1903, I. 508).

The following table contains the melting-points of the chlorides and amides of the acids :—

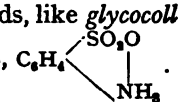
	Ortho.		Meta.		Para.	
	Chloride.	Amide.	Chloride.	Amide.	Chloride.	Amide.
Chloro-sulpho-.	28°	188°	Oil	148°	53°	143°
Bromo-sulpho-.	51°	186°	Oil	154°	75°	166°
Iodo-sulpho- .	51°	170°	23°	152°	84°	183°
Nitro-sulpho- .	67°	186°	60°	161°	Oil	181°

o-Iodo-chloride-benzol sulpho-chloride $ICl_2[2]C_6H_4[1]SO_2Cl$, m.p. 60°, is converted by sodium hydroxide into **iodoso-benzol-sulphonic acid** (B. **28,** 95).

m-Nitroso-benzol-sulphonic acid (B. **25,** 75).

Amido-benzol-sulphonic acids.—(1) On sulphonating aniline at 180° with fuming sulphuric acid (8–10 per cent. SO_3), the p-derivative constitutes the chief product. It is *sulphanilic acid*, important in the technology of dyes, and was discovered in 1845 by Gerhardt. The second sulpho-group enters the o-position with the formation of **1-aniline-2, 4-disulphonic acid** or **disulphanilic acid** ; a trisulphonic acid is not produced (B. **28,** 2143).

Amido-benzol-sulphonic acids are also produced (2) by reduction of nitro-benzol-sulphonic acids ; (3) by heating chloro-benzol-sulphonic acids with ammonia in the presence of copper salts (C. 1909, I. 477). (4) The sodium salts of phenyl-sulphaminic acids, on being heated to 170°–180°, transpose themselves into amido-benzol-sulphonates (C. 1907, I. 1792).

The amido-benzol-sulphonic acids, like *glycocoll* and *taurine*, can be regarded as cyclic ammonium salts,  .

The three amido-benzol-sulphonic acids dissolve with difficulty in water, alcohol, and ether. The (*ortho*)-acid either crystallises in anhydrous rhombohedra or in four-sided prisms containing $\frac{1}{2}H_2O$; these do not effloresce. It is best prepared by the reduction of p-bromo-aniline-o-sulphonic acid (B. **28,** R. 751 ; **29,** 1075 ; C. 1903, I. 508).

The (*meta*)-acid, called metanilic acid, and also important in the technology of dyes, crystallises in delicate needles or in prisms with $1\frac{1}{2}H_2O$, which effloresce.

p-Sulphanilic acid crystallises from hot water in rhombic plates with 1 molecule H_2O ; these effloresce in air. They are soluble in 112 parts H_2O at 15° (B. **14,** 1933). It yields a considerable quantity of quinone when oxidised with MnO_2 and H_2SO_4 or chromic acid. It yields aniline and not amido-phenol when fused with caustic potash ; unlike its isomerides, it is readily converted by bromine water into tribromo-aniline (B. **29,** R. 309).

The sodium-amido-benzol-sulphonates yield acetyl derivatives with acetic anhydride (B. **17,** 708 ; **39,** 1561), whereas the free acids are

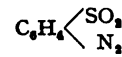
not in condition to do this. This fact argues for the ammonium-salt formula of the free acids.

In the o- and p-amido-benzol-sulphonic acids the sulpho-group is replaced by the nitro-group under the action of nitric acid, nitranilines being produced (A. **339**, 202).

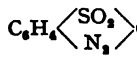
p-Phenylene-diamido-monosulphonic acid $C_6H_3(SO_3H)(NH_2)_2$ is produced by heating p-dichloro-benzol-sulphonic acid with ammonia in the presence of copper bronze (C. 1908, II. 1307).

Toluylene-diamido-sulphonic acids, see C. 1904, I. 1410.

Diazo-benzol-sulphonic-acid anhydrides, *cyclic diazides.*—Nitrous acid transforms the three amido-benzol-sulphonic acids into the anhydrides of the diazo-benzol-sulphonic acids (cp. C. 1898, I. 293) :



Diazo-benzol-sulphonic acid



Anhydride.

The hydrated sulpho-acids are not known ; they pass at once into anhydrides. The **dipotassium** and the **disodium** salts of the o- and p-diazo-benzol-sulphonic acids, $C_6H_4(SO_3Me)(N_2OMe)$, exist each in two forms, one of which belongs to the normal and the other to the iso-diazo-series. The **iso**-salts are produced on digesting the normal salts ; they give up nitrogen less readily, and do not combine, or at least with difficulty, with aromatic amines or phenols, to yield azo-dyes (B. **29**, 1059, 1388). **Primary potassium-iso-diazo-sulphonate** $C_6H_4(SO_3K)N_2OH+H_2O$ results on treating the corresponding dipotassium salt with acetic acid (B. **28**, 1386).

It is rather remarkable that, while otherwise it is only the ortho-compounds of the benzene di-derivatives which form inner anhydrides, *all three of the diazo-benzol-sulpho-acids are capable of anhydride formation.* They exhibit all of the reactions of the diazo-compounds.

The *diazide of sulphanilic acid*, p-diazo-benzol-sulphonic acid, consists of sparingly soluble white needles ; although relatively stable for a diazo-body, it sometimes explodes spontaneously (B. **34**, 11). Heated with absolute alcohol, it forms *benzol-sulphonic acid* ; with water the diazo-acid becomes *p-phenol-sulphonic acid* ; while with potassium sulphide the dipotassium salt of *p-thio-phenol-sulphonic acid* results. Concerning the effect of bleaching-lime upon diazo-benzol-sulphonic acids, see A. **330**, 1.

Amido-azo-benzol-sulphonic acids.—The diazides of sulphanilic acid and metanilic acid are used in the manufacture of *sulphurised azo-dyes.* The first group of this great class of dyes has received mention ; it comprises the amido-azo-compounds, which are insoluble or dissolve with difficulty in water. Upon introducing the sulpho-group into the amido-azo-derivatives it will be discovered that the solubility in general increases with the number of sulpho-groups. The alkali salts of the amido-azo-benzol-sulphonic acids constitute the dyes soluble in water. We shall meet with other groups of azo-dyes when we study the phenols : *oxyazo-compounds.* The *naphthalin-azo-compounds* and the *benzidin dyes*, containing the diphenyl residue, are especially important.

Arbitrary names are assigned these *dyes*, with the addition of the letters Y (yellow), O (orange), and R (red), whose number approxi-

mately expresses the intensity of the colour. They colour wool and silk directly, cotton after it has been mordanted.

Formation.—(1) The amido-azo-bodies are sulphurised. (2) The diazides of sulphonic acids are combined with bases.

Upon sulphonating amido-azo-benzol there results a mixture of amido-azo-benzol-mono- and disulphonic acids, known in commerce under the names *acid yellow* or *pure yellow*: $SO_3H[4]C_6H_4(1)N=N[1']C_6H_4[4']NH_2$ and $SO_3H[4]C_6H_4[1]N=N[1']C_6H_3[4']NH_2[3']SO_3H$ (B. **22,** 847). Being amido-bodies, the sulpho-acids are themselves capable again of diazotising and combination, whereby very valuable dyes have been obtained (compare *Biebrich scarlet*). Amido-azo-benzol-trisulphonic acid, see B. **33,** 1366.

The following azo-dyes have been made by combining the diazide of sulphanilic acid with dimethyl-aniline and diphenyl-amine, and the diazide of metanilic acid with diphenyl-amine:

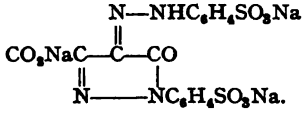
[4']-Dimethyl-amido-azo-benzol-[4]-sulphonic acid $SO_3H[4]C_6H_4[1]N=N[1]C_6H_4[4']N(CH_3)_2$, melting at 115°, consists of golden-yellow flakes (B. **10,** 528; **12,** 1490; **41,** 1187). Its sodium salt, as a dye, bears the names *tropæolin* O, *orange* III, and *helianthin*. It serves as a delicate indicator in alkalimetry; mineral acids convert the alkaline orange-coloured solution into pink. CO_2, H_2S, and acetic acid do not act on it in the cold (*Ch. Z.*, VI. 1249; B. **18,** 3290). By reduction *helianthin* yields sulphanilic acid and para-amido-dimethyl-aniline. Fuming nitric acid splits it up into diazo-benzol-sulphonic acid and 2, 4-dinitro-dimethyl-aniline (B. **38,** 3206; **41,** 1989).

[4']-Phenyl-amido-azo-benzol-[4]-sulphonic acid $SO_3H[4]C_6H_4[1]N=N[1]C_6H_4[4']NHC_6H_5$. Its sodium salt dyes wool and silk a beautiful orange, and as a dye is known by the names *tropæolin* OO, *orange* IV. It is used as an indicator in alkalimetry (B. **16,** 1989). By reduction it yields sulphanilic acid and p-amido-diphenyl-amine.

[4']-Phenyl-amido-azo-benzol-[3]-sulphonic acid is formed from metanilic acid, and bears the name *metanil yellow*.

Phenyl-hydrazin-sulphonic acids are produced upon reducing the diazides of aniline-sulphonic acids with sodium sulphite or stannous chloride (B. **22,** R. 216), and by the direct action of concentrated sulphuric acid upon phenyl-hydrazins (B. **18,** 3172).

Phenyl-hydrazin-p-sulphonic acid $C_6H_4.(NH.NH_2)SO_3H$ is not readily soluble in water. It is used in the preparation of tartrazin (Vol. I.), having the following constitution:



Hydrazo-benzol-m-disulphonic acid $SO_3H[3]C_6H_4[1]NH—NH[1]C_6H_4[3']SO_3H$ has been prepared by the reduction of m-nitro-benzol-sulphonic acid, and is converted into benzidin-disulphonic acid by hydrochloric acid (B. **21,** R. 323; **23,** 1053).

Sulphinic Acids.—*Formation*:—(1) By the action of zinc dust upon the ethereal solution of the sulphonic-acid chlorides. (2) From the latter and thio-phenol salts:

$$C_6H_5SO_2Cl+2C_6H_5SNa=C_6H_5SO_2Na+NaCl+(C_6H_5S)_2.$$

(3) By a straightforward reaction, sulphinic acids are produced by the action of Cu powder upon diazonium-salt solutions saturated with SO_2 (B. **32,** 1136):

$$C_6H_5N_2.SO_4H+SO_2+Cu=C_6H_5.SO_2H+N_2+SO_4Cu.$$

(4) Sulphinic acids are also produced from SO_2 and benzene in the presence of Al chloride, a reaction in which the compound $ClSO_2AlCl_2$ is formed as an intermediate product. The reaction is an extremely smooth one (B. **41,** 3315). In this case the phenol ethers yield also sulphoxides and sulphonium bases (C. 1908, II. 237). (5) By the action of SO_2, or SO_2Cl_2, upon phenyl-magnesium bromide (B. **87,** 2153; C. 1905, I. 1145). (6) From sulphones with sodium (B. **26,** 2813). (7) By the action of KCN or sodium arsenate upon benzol thio-sulphonates (B. **41,** 3351). (8) By decomposition of benzol-sulphydroxamic acids.

Behaviour.—The *sulphinic acids* are not very stable, and when heated with water split up into sulphonic acids and *disulphoxides.*

The air and oxidising agents (especially MnO_4K or BaO_2) convert them into sulphonic acids. By reduction, zinc dust, and sulphuric acid, the sulphinic acids are converted into thio-phenols.

Their salts unite with sulphur, forming thio-sulphonates. When fused with alkalies they decompose into benzenes and alkaline sulphites. By the action of thionyl chloride they yield sulphinic chlorides (B. **41,** 4114), and with acetic anhydride, sulphinic anhydride (B. **41,** 3323). With aldehydes the sulphinic acids combine to form **oxy-sulphones** $CH_3CH(OH)SO_2C_6H_5$; to $\alpha\beta$-unsaturated aldehydes, ketones, and carboxylic acids they add themselves like sulphurous acid with formation of **sulphones,** like $C_6H_5CH(SO_2C_6H_5)CH_2COOH$ (C. 1904, I. 874).

Benzol-sulphinic acid and quinone unite to unsym. **p-dioxy-diphenyl-sulphone** $(HO)_2[2,5]C_6H_3[1]SO_2C_6H_5$ (B. **27,** 3259); this also reacts with a number of other substances containing quinoid linkages (cp. B. **29,** 2019). Benzol-sulphinic acid also reacts with o- and p-dioxy-benzols, forming dioxy-diphenyl-sulphones, while phenol gives compounds like **oxy-diphenyl sulphide** $HOC_6H_4SC_6H_5$, and aniline chlorohydrate yields **amido-diphenyl sulphide** $H_2NC_6H_4SC_6H_5$ (B. **36,** 107).

The alkaline sulphinates form, with iodo-alkylene, mixed sulphones, and with chloro-carbonic esters they form the real sulphinic esters (B. **26,** 308, 430):

$$C_6H_5SO_2Na+ClCO_2C_2H_5 = C_6H_5SOO.C_2H_5+NaCl+CO_2.$$

With ferric chloride the sulphinic acids, in acid solution, form slightly soluble ferric salts, well adapted to the isolation of the sulphinic acids (C. 1909, I. 1649).

Benzol-sulphinic acid $C_6H_5.SO.OH$, m.p. 83°. **Zinc salt** $(C_6H_5SO_2)_2Zn+2H_2O$. **Ethyl ester,** sp. gr. 1·141 (20°), decomposes when it is heated.

Benzol-sulphinic anhydride $(C_6H_5SO_2)_2O$, m.p. 67°, deliquesces rapidly with formation of benzol-sulphonic acid and benzol-thio-sulphonic phenyl ester $C_6H_5SO_2SC_6H_5$.

Benzol-sulphinic chloride C_6H_5SOCl, colourless plates, m.p. 38°, fumes in air, and is rapidly decomposed by water, with regeneration of benzol-sulphinic acid.

o- and **p-Toluol-sulphinic acid** $C_6H_4[1](CH_3)[2]SOOH$, m.p. 80° and 85° (*J. pr. Ch.* **54,** 517; **56,** 213). For further homologues, see B. **32,** 1140. **Dimethyl-** and **diethyl-aniline-sulphinic acid** $R_2NC_6H_4SO_2H$ is formed by the action of thionyl chloride upon dimethyl- and diethyl-aniline (A. **310,** 137). **Benzol-disulphinic acid** $C_6H_4(SO_2H)_2$, see B. **35,** 2168; **36,** 189.

Benzol-seleninic acid C_6H_5SeOOH, m.p. 124°, by oxidation of phenyl diselenide with nitric acid, and by the action of HCl upon benzol-seleno-acid. On heating to 130° it passes into **benzol-seleninic anhydride** $(C_6H_5SeO)_2O$, m.p. 164° (C. 1909, II. 21).

Benzol-thio-sulphonic acid.—Its salts result from the chloride of benzol-sulphonic acid, and alkali sulphides, as well as from the interaction of benzol sulphinates and sulphur (B. **25,** 1477). With organic bases the thio-sulphonic acids often form easily crystallised salts (C. 1900, I. 611).

Disulphoxides or Esters of the Thio-sulphonic Acids.—**Alkyl** esters and **alkylene** esters of benzol-thio-sulphonic acid result from the interaction of the potassium salt with the corresponding bromides (B. **25,** 1477). **Phenyl-thio-sulphonic aceto-acetic ester** $C_6H_5SO_2S.CH(COCH_3)COOC_2H_5$, m.p. 56°, from chloraceto-acetic ester and potassium-benzol thio-sulphonate (C. 1900, II. 178).

Phenyl esters—*e.g.* $C_6H_5.SO_2.S.C_6H_5$—are obtained (1) by oxidising the thio-phenols with nitric acid; (2) by heating the sulphinic acids with water to 130°; (3) by oxidation of disulphides with hydrogen peroxide (B. **41,** 2838).

Benzol disulphoxide $C_6H_5.SO_2.S.C_6H_5$, m.p. 45°, is insoluble in water, but dissolves readily in alcohol and ether (**B. 20,** 2090).

Sulpho-benzol sulphide $(C_6H_5SO_2)_2S$, m.p. 133°, and **sulpho-benzol disulphide** $(C_6H_5SO_2)_2S_2$, m.p. 76°, **trisulphide,** m.p. 103°, result from the action of iodine and of chlorine upon potassium-benzol thio-sulphonate; also from benzol sulphinates and benzol thio-sulphinates with sulphur chlorides (B. **24,** 1141; *J. pr. Ch.* 2, **60,** 113).

Disulphones, like **diphenyl-sulphone** $C_6H_5SO_2.SO_2C_6H_5$, m.p. 194°, **phenyl-tolyl-disulphone** $C_6H_5SO_2.SO_2C_6H_4.CH_3$, m.p. 166°, **Ditolyl-disulphone** $CH_3C_6H_4SO_2.SO_2C_6H_4CH_3$, m.p. 212° with decomposition, are formed by transposition of sulphinates with sulpho-chlorides (C. 1899, II. 719). Also in small quantities, besides sulpho-acids, during the oxidation of benzol-sulphinic acids with MnO_4K (C. 1908, II. 1427). On heating with alkalies they decompose into a mixture of sulphinates and sulphonates.

Sulphoxides.—Mixed aromatic-aliphatic sulphoxides are formed from the aryl-alkyl sulphides by oxidation with H_2O_2 (B. **41,** 2836; C. 1909, I. 350), or from their dibromo addition products by the action of water.

Phenyl-sulphoxy-acetic acid $C_6H_5SOCH_2COOH$, m.p. 116°, is split up by heating with mineral acids into thio-phenol and glycolic acid.

Diphenyl-sulphoxide, *thionyl-benzol* $(C_6H_5)_2SO$, m.p. 70°, is produced (1) by the action of SO_2 or $SOCl_2$ upon benzenes in the presence of Al_2Cl_2 (B. **20,** 195; **27,** 2547); (2) by oxidation of diphenyl sulphide with H_2O_2 (B. **43,** 289); (3) by the action of thionyl chloride or diethyl sulphite upon phenyl-magnesium bromide (B. **43,** 1135). Potassium permanganate oxidises it to diphenyl-sulphone.

Diphenyl-selenium oxide $(C_6H_5)_2SeO$ has been prepared by oxi-

dising diphenyl selenide (*q.v.*), or from the dibromide of the latter (B. **29,** 424).

SULPHONES.—The *alkyl-aryl sulphones* are isomeric with the esters of the alkyl-sulphonic acids. They result from the sodium sulphinates and the alkylogens. The purely *aromatic* sulphones are obtained (1) by the action of SO_3 or chloro-sulphonic acid upon benzenes (together with sulphonic acids), $2C_6H_6+SO_3=(C_6H_5)_2SO_2+H_2O$; (2) by the distillation of sulphonic acids (together with hydrocarbons); (3) by the oxidation of the phenyl sulphide; (4) on heating benzol-sulphonic acids with benzenes and P_2O_5; (5) by the action of zinc dust, or aluminium chloride, upon a mixture of a sulphonic chloride and a benzene hydrocarbon:

$$C_6H_5SO_2Cl+C_6H_5CH_3 \longrightarrow \left.\begin{matrix} C_6H_5 \\ CH_3[1]C_6H_4[4] \end{matrix}\right\} SO_2 \longleftarrow C_6H_6+CH_3[1]C_6H_4[4]SO_2Cl.$$

The same phenyl-p-tolyl-sulphone results from benzol-sulphonic acid and toluol, as from p-toluol-sulphonic acid chloride and benzene, which would prove *that both groups are in union with sulphur, and that the latter is sexivalent* (B. **11,** 2181). (6) Nitro-substituted sulphones are readily formed from o- and p-chloro-nitro-benzols with sulphinates (B. **34,** 1150). (7) Oxy- and amido-substituted sulphones result from the union of sulphinic acids with quinone- and quinone-imine derivatives.

Phenyl-ethyl-sulphone $C_6H_5SO_2C_2H_5$, m.p. 42° and b.p. above 300°. **Phenyl-ethyl-sulphone alcohol** $C_6H_5.SO_2.CH_2.CH_2OH$, is a syrup formed from ethylene chloro-hydrin and sodium-benzene sulphinate, as well as by the action of concentrated sodium hydroxide upon **ethylene-diphenyl-disulphone** $C_6H_5SO_2.CH_2.CH_2.SO_2.C_6H_5$, m.p. 180°. Phenyl-sulphone-ethyl alcohol upon oxidation yields **phenyl-sulphone-acetic acid** $C_6H_5SO_2CH_2.CO_2H$, m.p. 112°; caustic potash resolves this into CO_2 and **phenyl-methyl-sulphone** $C_6H_5.SO_2.CH_3$, m.p. 88°. **Phenyl-sulphone acetamide** $C_6H_5SO_2CH_2CONH_2$, m.p. 156°, from sodium-benzol sulphinate and chloro-acetamide (C. 1905, I. 1134). **Phenyl-sulpho-aceto-nitrile** $C_6H_5SO_2CH_2CN$, m.p. 114°.

The hydrogen of the CH_2 group in the esters of phenyl-sulphone-acetic acid is replaceable by sodium, but not by alkyls (B. **22,** 1447; **23,** 1647; *J. pr. Ch.* 2, **60,** 96; C. 1905, II. 1784).

Phenyl-allyl-sulphone $C_6H_5SO_2.C_3H_5$ is an oil (A. **283,** 185).

The α- and β-phenyl-sulphone-propionic acids, melting at 115° and 123° (B. **21,** 89), as well as numerous other mixed fatty-aromatic sulphones of the greatest variety, have also been prepared.

Diphenyl-sulphone $(C_6H_5)_2SO_2$, *benzol-sulphone, sulpho-benzide,* melting at 128° and boiling at 276°, is formed by the distillation of benzol-sulphonic acid, and by the oxidation of the phenyl sulphide $(C_6H_5)_2S$ and *diphenyl sulphoxide* (see above); further, from benzol-sulphonic chloride $C_6H_5.SO_2Cl$ and mercury-diphenyl, as well as from benzol and benzol-sulphonic chloride or sulphuryl chloride with aluminium chloride (B. **26,** 2940). It is also obtained by the action of fuming sulphuric acid or SO_3 upon benzene. It is converted into benzol-sulphonic acid when digested with concentrated sulphuric acid. When heated with PCl_5, or in a current of chlorine gas, it is decomposed into chloro-benzol and the chloride of benzol-sulphonic acid.

With sulphur or selenium it forms the diphenyl-sulphone: *diphenyl*

sulphide or *diphenyl selenide* (B. **27,** 1761). Sodium converts it into sodium-benzol sulphinate and diphenyl (B. **26,** 2813). **o-** and **p-nitro-diphenyl-sulphone** $NO_2C_6H_4SO_2C_6H_5$ m.p. 147° and 143°; and 2, 4, 6-**trinitro-diphenyl-sulphone** $(NO_2)_3C_6H_2SO_2C_6H_5$, m.p. 233°, are formed from o- and p-nitro-chloro-benzol or picryl chloride with sodium-benzol sulphinate. *Diphenyl-selenone* $(C_6H_5)_2SeO_2$, melting at 155° and boiling at 271°, results on oxidising diphenyl-selenium oxide with potassium permanganate (B. **29,** 424). On heating alone it deflagrates, giving off its oxygen and forming a stable diphenyl selenide.

7. Phenols.

The phenols are derived from the aromatic hydrocarbons by the replacement of hydrogen of the benzene residue by hydroxyl. The phenols, like the alcohols, are distinguished as mono-, di-, and tri-hydric, according to the number of hydroxyl groups which have entered. All of the six hydrogen atoms in benzene can be replaced by hydroxyl groups. The phenols correspond to the tertiary alcohols, as they yield neither acids nor ketones upon oxidation. Their acid nature, distinguishing them from alcohols, is governed by the more negative nature of the phenyl group, and is enhanced by the entrance of more negative groups (see Picric acid; C. 1903, I. 326; II. 717). In contrast to the phenols, the aromatic alcohols, which are their isomerides, and have the hydrogen of the side-chains replaced by hydroxyl, approach the aliphatic alcohols in their behaviour.

Various representatives of the phenols have been found in the vegetable kingdom.

Some of them occur already formed as phenol-sulphonic acids in the urine of mammalia. In the organism of the latter many organic bodies are oxidised to phenols: benzene to phenol, bromo-benzol to bromo-phenol, aniline to amido-phenol, phenol to hydroquinone. In the decay of albumin the presence of phenols has also been established.

Phenols are produced in the dry distillation of wood, particularly beech-wood, turf, bituminous coal (B. **26,** R. 151), and anthracite coal. To isolate the phenols from coal-tar, shake the latter with caustic alkali, in which they are soluble. Acids liberate them from this solution, and then they can be purified by fractional distillation.

MONOHYDRIC PHENOLS.—In addition to the methods of formation just given, the following are worthy of note:

(1) The decomposition of the diazo-derivatives, especially their sulphates, with boiling water or copper sulphate solution.

(2) Fusion of the sulphonic acids with potassium or sodium hydroxide. This reaction was discovered in 1867 by Kekulé, Würtz, and Dusart, independently of each other:

$$C_6H_5.SO_3K + KOH = C_6H_5.OH + SO_3K_2.$$

In practice this method is used to obtain phenols from sulpho-acids, the operation being carried out in iron vessels.

The experiment in the laboratory is executed in a silver or nickel dish, the fusion supersaturated with sulphuric acid, and the phenol extracted by shaking with ether.

In fusing sulphonic acids or phenols containing halogens, the latter

are also replaced with formation of polyhydric phenols. Occasionally the sulpho-group splits off as sulphate and is replaced by hydrogen; thus, cresol-sulphonic acid yields cresol.

(3) The halogen benzene substitution products do not react with alkalies; but if nitro-groups are present at the same time, the halogens are replaced even by digesting with aqueous alkalies—this will occur the more readily if the nitro-groups be multiplied. In this respect they approach the acid chlorides:

$$\underset{\text{Picryl chloride}}{C_6H_2(NO_2)_3Cl} + H_2O = \underset{\text{Picric acid.}}{C_6H_2(NO_2)_3OH} + HCl$$

(4) The amido-group in the nitro-amido-derivatives can also be replaced by hydroxyl on boiling with aqueous alkalies; ortho- and para-nitranilines $C_6H_4(NO_2).NH_2$ (not meta-), yield their corresponding nitro-phenols. The ortho-dinitro-products react similarly.

(5) Small quantities of phenol can be obtained from benzene by the action of ozone, hydrogen peroxide (palladium hydride and water), and by shaking with sodium hydroxide and air (B. **14,** 1144). By the addition of oxygen to benzene through the instrumentality of aluminium chloride.

(6) By the *breaking down* of phenol-carboxylic acids, when their salts are subjected to dry distillation with lime.

(7) The *synthesis* of the higher phenols by introduction of alkyls into the benzene nucleus takes place readily on heating the phenols with alcohols and $ZnCl_2$ to 200° (B. **14,** 1842; **17,** 669; **27,** 1614; **28,** 407):

$$C_6H_5.OH + (CH_3)_2CH.CH_2.OH = (CH_3)_3CH[4]C_6H_4[1]OH.$$

Alkyl ethers of the phenols are simultaneously produced; methyl alcohol yields only phenyl-methyl ether $C_6H_5.O.CH_3$. Magnesium chloride (B. **16,** 792) and primary alkali sulphates (B. **16,** 2541) possess the same condensing power as $ZnCl_2$.

(8) Phenols, under the influence of concentrated sulphuric acid, take up unsaturated hydrocarbons—*e.g.* iso-amylene—and form alkyl phenols (B. **25,** 2649).

(9) The introduction of alkyl groups into the phenol nucleus by means of the aluminium or ferric chloride reaction is not simple (cp. B. **32,** 2424); the phenol ethers are more suitable. On ethylation of phenol by means of ether and aluminium chloride, see B. **32,** 2391.

Behaviour: Replacement of the Hydrogen Atoms.—(1) The character of the phenols, recalling the acids, expresses itself in the ease with which they form salts, particularly with the alkalies. The hydrogen of the hydroxyl group is also readily replaced (2) by alcohol radicles and (3) by acid radicles.

(4) The presence of an hydroxyl group in the place of an aromatic hydrogen atom renders more easy the substitution of other hydrogen atoms by chlorine, bromine, and the nitro-group.

(5) The phenols unite with the diazo-compounds, forming azo- and diazo-dyes: oxy-azo-derivatives.

(6) *Colour Reactions of the Phenols.*—On adding phenols (mono- or polyhydric) to a solution of KNO_2 (6 per cent.) in concentrated sulphuric acid, intense colorations arise; with common phenol we get first a

brown, then green, and finally a royal-blue colour (reaction of Liebermann) (see B. **17,** 1875). Dyes are produced in this manner; their character is as yet unexplained. They have been called **dichroïns** (B. **21,** 249). The phenols afford similar colours in the presence of sulphuric acid, with diazo-compounds and nitroso-derivatives. Ferric chloride imparts colour to the solutions of most phenols. Mercury nitrate, containing nitrous acid, colours nearly all the phenols red (reaction of Plugge) (B. **23,** R. 202).

Replacement of the Hydroxyl Group.—(7) When heated with zinc dust the phenols are reduced to hydrocarbons.

(8) The oxygen of the simple phenols is not very easily replaced by chlorine when phosphorus pentachloride acts upon them. Phenol itself has given the body $C_6H_5OPCl_4$. The pentachloride acts with greater ease upon the nitro-phenols, forming nitro-chloro-benzols.

(9) Phosphorus sulphide converts the phenols into thio-phenols.

(10*a*) The anilines result on heating with zinc ammonium chloride.

(10*b*) In the alkyl ethers of the nitro-phenols (as with the acid esters) we can replace the OH by NH_2, on heating with alcoholic ammonia.

(11) For the oxidation of the alkyl residues of homologous phenols, see below.

Nuclear Syntheses.—(1) Compare methods 7, 8, and 9, upon the replacement of the aromatic hydrogen atoms of the phenols by alkyl groups.

(2) The alkali salts of the phenols are converted by carbon dioxide, at higher temperatures, into the alkali salts of oxy-acids—*phenol-carboxylic acids* (compare salicylic acid).

(3) The phenols also yield *phenol-carboxylic acids* with carbon tetrachloride and sodium hydroxide.

(4) Oxy-aldehydes or phenol-aldehydes (see salicyl-aldehyde) are produced from phenols, chloroform, and caustic soda.

(5) The phenols condense with formaldehyde to *phenol alcohols* (see Saligenin).

(6) *Cumarins* (*q.v.*) are formed on heating phenols with malic acid and sulphuric acid.

(7) Dye-stuffs belonging to the *aurin* series, and derived from triphenyl-methane $CH(C_6H_5)_3$ (*q.v.*), are obtained from the phenols by their action upon benzo-trichloride $C_6H_5.CCl_3$.

(8) The so-called *phthaleïns* are combinations of phthalic acid and o-sulpho-benzoic anhydride with the phenols. Similar reactions occur with naphthalic anhydride (*q.v.*), succinic anhydride, and other anhydrides of dibasic carboxylic acids.

Reduction of the Phenols.—On conducting phenyl vapours mixed with excess of hydrogen over finely divided nickel at 215°–230°, the phenols are reduced to hexahydro-phenols (C. 1904, I. 279; see also B. **40,** 1286).

By reduction of phenol with alternating currents, cyclo-hexanone is produced (*J. pr. Ch.* 2, **38,** 65).

Breaking down of the Benzene Nucleus of the Phenols.—(1) By oxidation of phenol (*q.v.*). (2) By treating the phenols with chlorine, and then decomposing the chlorine addition products with alkalies.

BENZO-PHENOL, **Phenol,** *carbolic acid,* $C_6H_5.OH$, m.p. 43° and b.p.

183°; its specific gravity is 1·084 (0°). It is obtained from amido-benzol, from benzol-sulphonic acid, from the three oxy-benzoic acids, etc., by the methods previously described. It occurs already formed in *Castoreum* and in the urine of the herbivoræ.

Commercial phenol is a colourless, crystalline mass, which gradually acquires a reddish colour on exposure to the air (B. **27,** R. 790; C. 1909, II. 597). Pure phenol crystallises in long, colourless prisms. It possesses a characteristic odour, burning taste, and poisonous and antiseptic properties. It dissolves in 15 parts at 20°, and very readily in alcohol, ether, and glacial acetic acid. It is volatile with steam. Ferric salts impart a violet colour to its neutral solutions. Bromine water precipitates [2, 4, 6]-tribromo-phenol from even very dilute solutions. On introducing phenol into the organism, it occurs in the urine as phenol-glucuronic acid (Vol. I.) and as phenyl-sulphuric acid.

Diphenols $C_{12}H_8(OH)_2$, derivatives of diphenyl (*q.v.*), are produced on fusing phenol with caustic potash.

Diphenylene oxide is produced when phenol is distilled over lead oxide. *Aurin* results when it is heated with oxalic or formic acid and dehydrating agents (*q.v.*). Potassium permanganate oxidises phenol to inactive or meso-tartaric acid (Vol. I.). Mono-persulphonic acid oxidises it to pyrocatechin and hydroquinone (*J. pr. Ch.* 2, **68,** 486). Chlorine finally changes phenol to keto-chlorides, which are derived from di- and tetrahydro-benzol (B. **27,** 537). Chlorine and caustic soda convert phenol into trichloro-R-pentene-dioxy-carboxylic acid. The most important reactions of phenol have been previously described.

History.—Runge discovered(1834) phenol in coal-tar and called it carbon-oil acid, or carbolic acid. He also observed the physiological properties it possessed in common with creosote. Laurent, in 1841, first obtained it pure and gave it the names *hydrate de phényle* or *acide phénique*, from φαίνειν, to illuminate, probably because it occurs in the tar produced in the manufacture of illuminating gas. Gerhardt, who prepared it from salicylic acid, introduced the name phenol, indicating thereby that it was an alcohol. In 1867 Lister, of Glasgow, showed its great importance in surgery as a disinfectant.

Phenolates.—*Phenates, potassium phenate* C_6H_5OK, and *sodium phenate* C_6H_5ONa, are obtained by dissolving phenol in caustic potash or soda, evaporating the solution, and sharply drying the residue. Both salts dissolve readily in water (B. **26,** R. 150). Carbon dioxide sets phenol free from them; it is, therefore, not soluble in the alkali carbonates.

Calcium phenate $(C_6H_5O)_2Ca$, and **mercury phenate** $(C_6H_5O)_2Hg$. (See B. **29,** R. 178, for the compounds of the phenols with aluminium chloride; and see Salicylic acid for the action of CO_2 upon dry phenates.) **Aluminium phenate** $(C_6H_5O)_3Al$, by heating phenol with Al. It is a glassy mass, melting about 265° (C. 1906, II. 114). On combinations of phenols with Al chloride, see B. **29,** R. 178; with nitrogen bases, B. **35,** 1207).

Homologous Phenols.—It is strange that the *cresols*, as well as other higher phenols, cannot be oxidised by the chromic acid mixture: *the OH-group prevents the oxidation of the alkyl groups by chromic acid.* If, however, the phenol-hydrogen is replaced by alkyls, or acid

radicles (in the phenol ethers and esters), then the oxidation of the alkyl does take place with the production of ether acids or ester acids.

The readily prepared sulphuric, or phosphoric, acid esters of the homologous phenols are best adapted for oxidation with an alkaline permanganate solution (B. **19,** 3304), whereas the free phenols are completely destroyed by this reagent (compare oxidation of phenol, above).

The oxidation of the alkyls in the sulpho-acids of the homologous phenols is similarly influenced by the sulpho-group. In general, ***negative atoms, or groups, prevent the oxidation of alkyls in the ortho-position by acid oxidants,*** whereas alkaline oxidants—*e.g.* $KMnO_4$—do precisely the reverse, in that they first oxidise the alkyl group holding the ortho-position (A. **220,** 16). The methyl groups of the methyl-phenols, such as the cresols and xylenols, are converted by molten alkalies, with the addition of PbO or PbO_2 (B. **89,** 794), into carboxyl groups, and there result oxy-benzoic acids, oxy-toluic acids, oxy-phthalic acids, etc. (compare the like behaviour of the homologous *pyrrols* and *indols*).

p-Alkylated halogen phenols are oxidised by nitric acid to so-called quinitrols and quinols, which substances are dealt with in connection with pseudo-phenol bromides and methylene-quinones in the chapter on "*Phenol Alcohols.*"

Other transposition reactions are given above. The liquid homologous phenols are particularly characterised by the melting-points of their benzoyl esters; therefore these will be given in connection with the various members.

1. **Cresols,** *oxy-toluols,* $CH_3.C_6H_4OH$.—The three isomerides occur in coal-tar and beechwood tar.

They are obtained from the toluidins by method I., and from the toluol-sulphonic acids by method II. They have a similar odour, but it is more disagreeable than that of phenol. They are less poisonous, and are disinfectants. They are changed to toluol when heated with zinc dust. Sodium and carbon dioxide produce the corresponding cresotinic acids.

See above for their behaviour towards molten caustic potash and other oxidising agents. o-Cresol is obtained from carvacrol, and the m-body from thymol (see below). The latter is also prepared from the dibromide of synthetic β-methyl-keto-R-hexene (*q.v.*) by the elimination of hydrogen bromide (A. **281,** 98).

o-Cresol, [1, 2]-*oxy-toluol,* m.p. 31°, b.p. 188°
m-Cresol, [1, 3]-*oxy-toluol,* ,, 4°, ,, 201°
p-Cresol, [1, 4]-*oxy-toluol,* ,, 36°, ,, 198°.

Ferric chloride colours o-cresol blue. The crude cresols are used as disinfectants: *creolin* is a solution of the crude cresols in alkalies; *cresolin* is a solution of the same in resin soaps; while *lysol* is a solution of crude cresols in oline soaps. See B. **14,** 687, for the behaviour of the cresols in the animal organism.

2. **Phenols** C_6H_3OH.—Oxy-dimethyl-benzols and oxy-ethyl-benzol. The six possible **xylenols** $C_6H_3(CH_3)_2.OH$ have been prepared.

Ethyl-phenols $C_6H_4(C_2H_5).OH$.—From the ethyl-benzol-sulphonic acids (B. **27**, R. 189).

o-Ethyl-phenol, liquid, b.p. 203°; benzoyl compound, m.p. 39°
m-Ethyl-phenol, ,, ,, 214°; ,, ,, ,, 52°
p-Ethyl-phenol, m.p. 45°, ,, 215°; ,, ,, ,, 59°.

3. **Phenols** $C_9H_{11}.OH$.—**Mesitol** $C_6H_2(CH_3)_3.OH$, from amido-mesitylene and mesitylene-sulphonic acid, m.p. 68° and b.p. 220°. [1]OH[2,4,5]-**Pseudo-cumenol** $C_6H_2(CH_3)_3.OH$, from pseudo-cumene-sulphonic acid, m.p. 73° and b.p. 232° (B. **17**, 2976). On the bromination products of pseudo-cumenol, and the formation of pseudo-phenol bromides, insoluble in alkalies, see "*Phenol Alcohols.*"

m-n-Propyl-phenol, from iso-safrol, m.p. 26° and b.p. 228° (B. **28**, 1162). **p-n-Propyl-phenol** boils at 232°. **p-Iso-propyl-phenol** melts at 61°, and boils at 229°. It is also produced along with hydroquinone on decomposing diphenol-β-propane $(CH_3)_2C(C_6H_4OH)_2$ (from the action of fuming hydrochloric acid on acetone and phenol), with molten caustic potash (B. **25**, R. 334).

4. **Phenols** $C_{10}H_{13}.OH$.—There are twenty possible isomerides. Thymol and carvacrol merit notice. They occur in vegetable oils. Both are derivatives of ordinary p-cymol, and contain the iso-propyl group.

Thymol, when heated with P_2O_5, breaks down into propylene and m-cresol; while carvacrol, under similar treatment, yields propylene and o-cresol.

Thymol = [3]-Methyl-[6]-iso-propyl-phenol $C_3H_7[6]C_6H_3\begin{cases}[1]OH\\[3]CH_3\end{cases}$

Carvacrol = [2]-Methyl-[5]-iso-propyl-phenol $C_3H_7[5]C_6H_3\begin{cases}[1]OH\\[2]CH_3\end{cases}$

Thymol, melting at 44° and boiling at 230°, crystallises in large, colourless plates. It exists with cymol $C_{10}H_{14}$, and thymol $C_{10}H_{16}$, in oil of thyme (from *Thymus vulgaris*), and in the oils of *Ptychotis ajowan* and *Monarda punctata*. To obtain the thymol, shake these oils with potassium hydroxide, and from the filtered solution precipitate thymol with hydrochloric acid. It is artificially prepared from nitro-cumin-aldehyde (*q.v.*), as well as from dibromo-menthone, by the splitting-off of hydrogen bromide (B. **29**, 420). It has a thyme-like odour and answers as an antiseptic.

Ordinary cymol is obtained by distilling it with P_2S_5. Thymoquinone (*q.v.*) is produced in its oxidation.

Iodine and caustic potash convert thymol into **di-iodo-di-thymol,** a diphenyl derivative which has been substituted for iodoform under the names *aristol* and *annidalin*.

On the processes of iodination and bromination of thymol, see C. 1903, I. 766.

Carvacrol, cymo-phenol, melting at 0° and boiling at 236°, isomeric with thymol, occurs already formed in the oil of certain varieties of satureja, also in *Briganum hirtum*, and is obtained from an isomeric *carvol*, a dihydro-cymol derivative (*q.v.*) contained in the oil of *Carvum carvi*, and certain other oils, when it is heated with glacial phosphoric acid (B. **19**, 12). It is further prepared by heating camphor with

iodine ($\frac{1}{5}$ part), using a return condenser. It is made artificially from cymol-sulphonic acid (B. **11,** 1060).

Distillation with P_2S_5 converts carvacrol into cymol and **thio-carvacrol** $C_{10}H_{13}.SH$.

s-Carvacrol $(CH_3)[3](CH_3)_2CH[5]C_6H_3[1]OH$ melts at 54° and boils at 241° (B. **27,** 2347). **Methyl-p-norm.-propyl-phenol** $(CH_3)[2]C_3H_7[5]C_6H_3OH$, from the corresponding sulpho-acid, boils at 240° (B. **29,** R. 417).

p-Tertiary butyl-phenol $(CH_3)_3C[4]C_6H_4[1]OH$, melting at 98° and boiling at 237°, is obtained from isobutyl alcohol, phenol, and zinc chloride (B. **24,** 2974). Oxidised with MnO_4K, it gives trimethyl-pyro-racemic acid and trimethyl-acetic acid (A. **327,** 201).

p-Tertiary amyl-phenol $(CH_3)_2(C_2H_5)C[4]C_6H_4[1]OH$, melting at 93° and boiling at 266°, results from the action of $ZnCl_2$ upon iso-amyl alcohol or tertiary amyl alcohol, and from iso-amylene, phenol, acetic acid, and sulphuric acid (B. **28,** 407). Oxidised with MnO_4K, it gives dimethyl-ethyl-pyro-racemic acid and dimethyl-ethyl-acetic acid (A. **327,** 201).

Diethyl-phenols, tetra-ethyl-phenol (B. **22,** 317; **32,** 2392).

Tetramethyl-phenols (B. **15,** 1852; **17,** 1916; **18,** 2842; **21,** 645, 907).

Pentamethyl-phenol, m.p. 125°, b.p. 267° (B. **18,** 1826).

Derivatives of the Monohydric Phenols.

The behaviour of the phenols was given under the example selected—ordinary phenol. Because this can be obtained with comparative ease, more derivatives of it, than of its homologues, have been prepared. In the following pages the derivatives of the homologues will only be brought forward and discussed in case they possess theoretical or practical value, and then in connection with the compounds of the corresponding phenol.

Phenol-alcohol Ethers.—(1) Like the ethers of the aliphatic alcohols, they result from the interaction of alkyl iodides and phenates. The phenol is digested with caustic potash, and the alkyl iodide, or methyl chloride, is conducted over sodium phenate heated to 200° (B. **16,** 2513).

(2) By heating a mixture of the alkali salts of the phenols with an excess of alkyl sulphates, in aqueous or alcoholic solution (B. **19,** R. 139).

(3) Together with hydrocarbons on decomposing benzol-diazo-compounds with alcohols (B. **25,** 1973).

(4) By heating phenyl-carbonic alkyl ester with elimination of CO_2:

$$C_6H_5OCOOCH_3 = C_6H_5OCH_3 + CO_2$$

(B. **42,** 2237).

(5) The phenols are converted at ordinary temperatures by diazo-methane, with evolution of nitrogen, into their methyl ethers (B. **28,** 857):

$$C_6H_5OH + CH_2N_2 = C_6H_5OCH_3 + N_2.$$

Dimethyl sulphate $(CH_3)_2SO_4$, p-toluol-sulphonic ester, and other bodies have been recommended as practical alkylators for phenols (A. **327,** 120; B. **27,** R. 955).

(6) By heating the phenol ethers of phenol-carboxylic acids with lime or baryta:

$$\underset{\text{Anisic acid}}{CO_2H[1]C_6H_4[4]OCH_3} \xrightarrow{-CO_2} \underset{\text{Anisol.}}{C_6H_5OCH_3}$$

Boiling with alkalies does not change the phenol ethers. Only after long heating with alcoholic potash to a high temperature does phenol form by disintegration (B. **34,** 1812). The ethers of multivalent phenols are partly saponified; veratrol produces guajacol (C. 1898, I. 456). Heating with HI, HBr, or HCl breaks up most phenyl-alkyl ethers into their generators:

$$C_6H_5OCH_3 + HI = C_6H_5OH + CH_3I.$$

This easy detachment of CH_3I and C_2H_5I, on heating phenol ethers with concentrated HI, may be used for the quantitative determination of the number of methoxyl or ethoxyl groups in a compound, the iodine compounds being converted into silver iodide in an alcoholic silver nitrate solution, and weighed (Zeisel, M. **6,** 989; **7,** 406). The phenol ethers are also decomposed by Al_2Cl_6 (B. **25,** 3531); PCl_5 only chlorinates the nucleus (B. **28,** R. 612). With Cl, Br, I, HNO_3, and H_2SO_4 the phenol ethers behave like aromatic hydrocarbons.

Anisol, methyl-phenyl ether $C_6H_5.O.CH_3$, is produced by distilling anisic or p-methyl-salicylic acid. It boils at 152°; its specific gravity at 15° is 0·991. It is not reduced by zinc dust (C. 1904, I. 1005).

Phenetol, ethyl-phenyl ether $(C_6H_5).O.C_2H_5$, b.p. 172°, has the specific gravity 0·9822(0°). The *iso-amyl ether* boils at 225°.

Bromethyl-phenyl ether $BrCH_2.CH_2.O.C_6H_5$ melts at 39° (*J. pr. Ch.* 2, **24,** 242).

Bromethenyl-phenyl ether $BrCH:CHOC_6H_5$, b.p.$_{15}$ 166°, from acetylene dibromide with potassium phenol; when treated with alcoholic potash it gives **phenoxy-acetylene** $C_6H_5.OC\equiv CH$, b.p.$_{35}$ 75°, an easily decomposed oil, which readily forms normal acetylene salts $C_6H_5OC:CAg$, $(C_6H_5OCC)_2Cu_2$, C_6H_5OCCNa.

Phenol-methylene ether $CH_2(OC_6H_5)_2$, m.p. 81°, b.p. 165° (B. **46,** 2789). **Phenol-ethylene ether, glycol-diphenyl ether** $C_6H_5OCH_2CH_2OC_6H_5$, m.p. 95°, is isomeric with phenol-acetol $(C_6H_5O)_2CHCH_3$, m.p. 10°, b.p. 175°, obtained from potassium phenol, with aldehyde chloride (C. 1900, I. 813). **Glycol-monophenyl ether,** b.p.$_{80}$ 165° (B. **29,** R. 289). **Glycerine-monophenyl ether** $C_6H_5OCH_2.CHOH.CH_2OH$, m.p. 70°, is formed by heating phenol with glycerine and sodium acetate (M. **29,** 951), or by adding water to **phenyl-glycidic ether** $C_6H_5OCH_2\overset{O}{\diagup\diagdown}CH—CH_2$, b.p. 242°, obtained besides glycerine-diphenyl ether, m.p. 82°, by transformation of sodium phenyl with epichloro-hydrin (C. 1908, I. 2032; 1910, I. 1134).

Phenoxalkylamines.—β-Phenoxethylamines $NH_2.CH_2.CH_2.O.C_6H_5$, b.p. 228° (B. **24,** 189). **γ-Phenoxy-propylamine** $NH_2.CH_2.CH_2.CH_2.O.C_6H_5$, b.p. 241° (B. **24,** 2637). **δ-Phenoxy-butylamine** $NH_2CH_2CH_2CH_2CH_2OC_6H_5$, b.p. 255° (B. **24,** 3232).

Phenol ethers of aldehyde alcohols, ketone alcohols, and alcohol acids have been obtained from the corresponding chlorinated aldehydes, ketones, and carboxylic acids, by the action of sodium phenate:

Phenoxy-acetaldehyde $C_6H_5O.CH_2.CHO$, b.p. 119° (30 mm.) (B. **28,** R. 295).

Phenoxy-acetone, *phenacetol* $C_6H_5O.CH_2.CO.CH_3$, b.p. 230°, is condensed by concentrated sulphuric acid to *methyl cumarone* (*q.v.*) (B. **28,** 1253; **35,** 3553).

Phenoxy-acetic acid $C_6H_5O.CH_2.COOH$, m.p. 96°, is isomeric with almond acid $C_6H_5CH(OH).COOH$. It results from monochloracetic acid and potassium phenate at 150°, as well as from the oxidation of phenoxy-acetaldehyde. It is a strong antiseptic (B. **19,** 1296; **27,** 2796).

Phenoxy-acetyl chloride $C_6H_5OCH_2COCl$, b.p.$_{60}$ 169° (see B. **35,** 3560).

Diphenoxy-acetic acid $(C_6H_5O)_2CHCO_2H$, m.p. 91° (B. **27,** 2796). *α*- and *γ*-**Phenoxy-butyric acid** melt at 99° and 60° (B. **29,** 1421). For homologous *α*-phenoxy-aliphatic acids, see B. **33,** 924, 1249.

α-**Phenoxy-aceto-acetic ester** $CH_3.CO.CH(OC_6H_5)CO_2C_2H_5$, from sodium phenate and *α*-chloraceto-acetic ester, is a thick oil. Concentrated sulphuric acid condenses it to **methyl-cumarilic ester. Phenoxy-fumaric ester** $C_6H_5OC(COOR):CHCO_2R$, from sodium phenol and acetylene-dicarboxylic ester (C. 1900, II. 1210).

Phenol Ethers.—Phenyl ether $(C_6H_5)_2O$, **diphenyl oxide,** melting at 28° and boiling at 252°, is produced by distilling copper benzoate (together with benzoic phenyl ether) and digesting diazo-benzol sulphate with phenol (B. **25,** 1973); also by heating phenol with zinc chloride to 350°, or, better, with aluminium chloride (B. **14,** 189). It crystallises in long needles, and possesses an odour resembling that of geraniums. It dissolves readily in alcohol and ether. It is not reduced on heating with zinc dust or hydriodic acid.

Nitrated phenyl ethers have been obtained by the interaction of the corresponding nitro-haloid benzols and the potassium salts of phenols: *o-Nitro-phenyl ether* $C_6H_5O.C_6H_4NO_2$ boils at 235° (60 mm.). *o, o'-Dinitro-phenol ether* $(NO_2.C_6H_4)_2O$ melts at 114° (B. **29,** 1880, 2084; C. 1903, I. 634).

Acid Esters of Phenol.—The *acid esters* are obtained by acting with acid chlorides or anhydrides upon the phenols or their salts; also by digesting the phenols with acids and $POCl_3$. To effect the substitution of all the hydroxyl-hydrogen atoms in the polyhydric phenols by acetyl groups, it is recommended to heat them with acetic anhydride and sodium acetate. On boiling with alkalies, or even with water, they, like all esters, break down into their components.

Esters of Inorganic Acids.—*Phenyl-sulphonic ester* is not known in a free state. Its **sodium salt** $NaSO_2OC_6H_5$ results from the action of SO_2 upon sodium phenate. Methyl iodide converts it into **methyl-sulphonic phenyl ester** $CH_3SO_2OC_6H_5$ (cp. B. **25,** 1875). Sulphonic aryl ester salts are also formed from phenols with sodium disulphite; they are distinguished for their reacting power; in some, the OSO_2Na group is replaced by NH_2 on heating with ammonia (C. 1901, II. 1136).

Phenyl-sulphuric acid $C_6H_5.O.SO_3H$ is not known in a free state; when liberated from its salts by concentrated hydrochloric acid, it immediately breaks down into phenol and sulphuric acid. Its **potassium salt** $C_6H_5.O.SO_3K$ forms flakes, not very soluble in cold water, and occurs in the urine of herbivorous animals, and also in that of man and

the dog after the ingestion of phenol. It is synthetically prepared, like other phenols, on heating potassium phenoxide with an aqueous solution of potassium pyro-sulphate (B. **9**, 1715); also from phenol and chloro-sulphonic acid by means of pyridin in CS_2 solution, and subsequent treatment with KOH (C. 1901, I. 313).

The phenyl-sulphuric acids are very stable in aqueous and alkaline solution; upon digesting with mineral acids, however, they are very rapidly decomposed. When potassium-phenyl sulphate is heated in a tube, it passes quietly into potassium-p-phenol sulphonate.

Phenyl Esters of the Phosphoric Acids.—These arise in the action of PCl_3 and $POCl_3$ (A. **239**, 310; **253**, 120; B. **30**, 2369):

Phenyl-phosphorous chloride . .	$C_6H_5O.PCl_2$,	boils at	90° (11 mm.)
Diphenyl-phosphorous chloride . .	$(C_6H_5O)_2PCl$,	,,	172° ,,
Triphenyl phosphite	$(C_6H_5O)_3P$,	,,	220° ,,
Phenyl-phosphoric chloride . .	$(C_6H_5O)POCl_2$,	,,	121° ,,
Diphenyl-phosphoric chloride . .	$(C_6H_5O)_2POCl$,	,,	195° (14 mm.)
Triphenyl phosphate, m.p. 45° . .	$(C_6H_5O)_3PO$,	,,	245° (11 mm.)

The last of these is best obtained by shaking up an alkaline phenol solution with phosphorus oxy-chloride.

The two phenyl-phosphorous chlorides take up chlorine:

Phenyl-phosphoric tetrachloride . .	$C_6H_5OPCl_4$
Diphenyl-phosphoric trichloride . .	$(C_6H_5O)_2PCl_3$

On phenol sulpho-phosphates, *e.g.* triphenyl sulpho-phosphate $(C_6H_5O)_3PS$, m.p. 53°, see B. **31**, 1094.

Phenyl Silicates (B. **18**, 1679).

Phenyl Esters of Monocarboxylic Acids.—**Phenyl formate** (*J. pr. Ch.* 2, **31**, 467). **Phenyl-ortho-formic ester** $CH(O.C_6H_5)_3$ is formed by boiling phenol with sodium hydroxide and chloroform. It melts at 71° and distils at 265°, under 50 mm. pressure (B. **18**, 2656).

Phenyl acetate $CH_3.COOC_6H_5$ boils at 195° (B. **18**, 1716). **Ortho-acetic phenyl ester** $CH_3C(OC_6H_5)_3$ melts at 98° (B. **24**, 3678).

Phenyl Carbonates.—The free phenyl-carbonic acid is not known. The opposite is true of **sodium-phenyl carbonate** $C_6H_5OCO_2Na$. It is produced when CO_2 acts upon sodium phenoxide (under pressure). It is a white hygroscopic powder, decomposed again by water. When heated under pressure to 120°–130°, **sodium salicylate** $HOC_6H_4CO_2Na$ results, just as phenol-sulphonic acid is obtained from phenyl-sulphuric acid (see above). Heated to 120°–130° under pressure, it transposes to **sodium-phenol-o-carboxylic acid** $NaOC_6H_4COOH$. When heated to 190° with sodium phenate, sodium-phenyl carbonate yields *disodium salicylate* and phenol (B. **38**, 1375).

Phenyl Carbonate.—The carbonic acid ester $CO(O.C_6H_5)_2$ is produced on heating phenol and phosgene gas $COCl_2$ to 150°. It is readily obtained by leading phosgene gas into the aqueous solution of sodium phenylate (*J. pr. Ch.* **17**, 139; B. **17**, 287). It crystallises from alcohol in shining needles, and melts at 78°. It yields *sodium salicylate* when heated to 200° with sodium hydroxide. Urea results if it be heated with ammonia (B. **23**, 694).

Mixed carbonates containing phenol and alkyls—*e.g. phenyl-ethyl carbonate* $CO_3(C_2H_5)(C_6H_5)$—are produced by the action of chloro-

formic esters upon the sodium salts of the phenols, or of alcohols upon chloro-formic phenyl ester, obtained from phosgene with phenols (C. 1899, II. 825); they also form on heating phenyl carbonate with the alcohols in the presence of urea (C. 1898, II. 476). On heating, they split off CO_2 and pass into phenol-alkyl ether (B. **42**, 2237).

Diphenyl-thio-carbonic ester $C_6H_5OCSOC_6H_5$ (B. **27**, 3410; C. 1906, II. 1760). **Phenyl-carbaminate, phenyl-urethane,** $NH_2COOC_6H_5$, melts at 141° (B. **33**, 51; A. **244**, 43). **Phenyl-carbamic phenyl ester** $C_6H_5NHCO_2C_6H_5$, from carbanile and phenol, m.p. 124° (B. **18**, 875; **27**, 1370). **Diphenyl-thio-carbamic phenyl ester** $(C_6H_5)_2NCOOC_6H_5$, m.p. 105°, from diphenyl-urea chloride and phenol. **Phenyl-carbaminic phenyl ester** $C_6H_5O.CSNHC_6H_5$, m.p. 148°, is produced on heating phenyl-mustard oil with phenol to 280° (B. **29**, R. 177).

Phenyl-imido-carbonic phenyl ester $C_6H_5N : C(OC_6H_5)_2$, m.p. 136°, is obtained from iso-cyano-phenyl chloride and sodium phenate (B. **28**, 977).

Phenyl-allophanic ester $CO\langle^{NH_2}_{NH.CO_2.C_6H_5}$ is produced by conducting cyanic acid vapours into anhydrous phenol. A crystalline mass.

Phenyl Esters of Dicarboxylic Acids. — **Phenyl-oxalic ester** $(COOC_6H_5)_2$, m.p. 136°, b.p.$_{15}$ 191° (B. **35**, 3437). **Malonic diphenyl ester,** m.p. 50° (B. **35**, 3455).

Ethyl-phenyl-oxalic ester $COOC_2H_5.COOC_6H_5$, b.p. 236°, is obtained from ethyl-oxalic chloride (Vol. I.). The **succinic ester** melts at 118° and boils at 330°. **Phenyl-fumaric ester,** m.p. 161°, decomposes when distilled slowly into CO_2, phenyl-cinnamic ester (*q.v.*), and stilbene (*q.v.*) (B. **18**, 1948).

Phenol Substitution Products.

Phenol Haloids.—*Formation*:—(1) Chlorine and bromine react readily with phenols; this is exemplified in bromine precipitating phenol quantitatively from its aqueous solutions as [1 OH,2, 4, 6]-tribromo-phenol. Chlorine and bromine enter the ortho- and para-positions; there result at first the [1, 2]- and [1, 4]-mono-, then the [1, 2, 4-] di-, and finally the [1, 2, 4, 6]-tri-substitution products. At 150°–180°, by action of chlorine or bromine vapours, abundant quantities of o-chloro- and o-bromo-phenol (B. **27**, R. 957) are produced. Sulphuryl chloride, which easily chlorinates the free phenols (but not their ethers), yields p-chloro-phenol (C. 1898, I. 1051).

The iodo-derivatives are formed by adding iodine and iodic acid to a dilute potassium hydroxide solution of phenol (Kekulé, A. **137**, 161):

$$5C_6H_5OH + 2I_2 + IO_3H = 5C_6H_4I.OH + 3H_2O,$$

or by the action of iodine and mercuric oxide. Di-iodo-phenol is the chief product in the latter case.

(2) In the phenol-sulphonic and phenol-carboxylic acids the action of chlorine and bromine leads to the replacement of the sulpho- and carboxyl groups in the o- and p-positions as phenyl hydroxyl by halogens (B. **42**, 4361).

(3) From substituted anilines, by the replacement of NH_2 by OH, which may be brought about by the diazo-compounds; this reaction leads to pure mono-haloid phenols. (4) From the nitro-phenols by

replacing the nitro-group with halogens (effected through the amido- and diazo-derivatives). (5) By distilling substituted oxy-acids with lime or baryta.

Behaviour.—(1) The introduction of halogen atoms considerably increases the acid character of phenol; thus, trichloro-phenol readily decomposes the alkaline carbonates.

(2) When fused with potassium hydroxide, the halogen is replaced by the hydroxyl group. In this reaction it frequently happens, especially at high temperatures, that not the corresponding isomerides, but rather the more stable derivative, results; for example, all the bromo-phenols yield resorcin. The caustic potash fusion is, therefore, not applicable in determining constitution.

(3) Sodium amalgam causes the replacement of the halogen atoms by hydrogen.

(4) By the action of HNO_2 upon bromine-substituted phenols the Br atoms, in o- or p-position to the hydroxyl, are easily replaced by nitroyl (*J. pr. Ch.* 2, **61**, 561; A. **333**, 346).

Monohaloid Phenols.—The monochloro-phenols in particular are characterised by a disagreeable, very adherent odour. The bromo- and iodo-phenols, being attacked at a lower temperature than the chloro-derivatives, are changed, on fusing with potash, into the corresponding dioxy-benzols. The higher the temperature rises in the fusion of the o- and p-compounds, the greater will be the yield of resorcin or m-dioxy-benzol; the three isomeric monochloro-phenols yield resorcin:

	Ortho-		Meta-		Para-		
	M.p.	B.p.	M.p.	B.p.	M.p.	B.p.	
Chloro-phenol	7°	176°	28°	212°	41°	217°	
Bromo-phenol	liquid	195°	32°	236°	66°	238°	
Iodo-phenol	43°	..	40°	..	94°	..	(B. **20**, 3019).

See B. **29**, 997, 1409, 2595, for the **iodo-anisols** and **phenetols.**

Polyhaloid Phenols.—In the direct substitution the [2, 4]-di- and [2, 4, 6]-trihaloids are produced quite readily. On prolonged chlorination of the phenols a tetrachloro-phenol is finally obtained (C. 1903, I. 232). As to the iodination of phenol, see C. 1901, I. 1004; 1902, I. 638, 668.

[2, 4]-Dichloro-phenol, m.p. 43°, b.p. 210°
[2, 5]-Dichloro-phenol, „ 58°, „ 211°
[2, 4]-Dibromo-phenol „ 40°, „ ..
[2, 4]-Di-iodo-phenol, „ 72°, „ ..
[2, 3, 4, 6]-Tetrachloro-ph., m.p. 70° (B. **37**, 4013).
[2, 3, 4, 6]-Tetrabromo-ph., „ 120° (A. **187**, 209).
[2, 4, 6]-Trichloro phenol, m.p. 68°, b.p. 244°
[2 4, 6]-Tribromo-phenol, „ 92° ..
[2, 3, 5]-Tribromo-phenol, „ 92°, (B. **39**, 4251)
[2, 4, 6]-Tri-iodo-phenol, „ 156° ..
[3, 5, 6]-Tri-iodo phenol, „ 114° (C. 1904, I. 266)
Pentachloro-ph., „ 186° (B. **28**, R. 150)
Pentabromo-ph. „ 225°.

The silver salts of tribromo-phenol, as well as of some other poly-brominated phenols, exist in an unstable orange-red, and a stable white, modification. The cause of this allotropy is still unexplained (B. **40**, 4875).

The tri-, tetra-, and pentachloro- and bromo-phenols take up chlorine and bromine, becoming chlorinated and brominated *oxodi-* and *oxotetra-hydra-benzols*, from which the halogen phenols are regenerated by reduction (B. **37**, 4010). On further bromination tribromo-phenol gives **bromine tribromo-phenol** $C_6H_2Br_4O$, m.p. 148° (A. **302**,

133; C. 1902, II. 358), which is easily reconverted into tribromo-phenol, but is transposed into **tetrabromo-phenol** $C_6Br_4H(OH)$ by concentrated SO_4H_2, and yields dibromo-quinone on digesting with lead acetate; it must therefore be regarded as *p-keto-dihydro-tetra-bromo-benzol* (B. **38**, 675; C. 1902, I. 469):

$$HO\frac{Br\ H}{Br\ H}Br \longrightarrow O\frac{Br\ H}{Br\ H}Br_2 \longrightarrow O\frac{Br\ H}{Br\ H}O.$$

HNO_3 oxidises trichloro-phenol into dichloro-quinone (C. 1908, I. 1776).

NITRO-PHENOLS.

The phenols, like the anilines, are very readily nitrated. The entrance of the nitro-groups increases their acid character very considerably. All nitro-phenols decompose alkaline carbonates (but see C. 1898, II. 596).

Trinitro-phenol is a perfect acid in its behaviour; its chloro-anhydride $C_6H_2(NO_2)_3Cl$ reacts quite readily with water, re-forming trinitro-phenol. The benzene nucleus of the nitro-phenols is capable of ready substitution with the halogens; whereas the nitro-hydrocarbons are chlorinated with difficulty.

The nitro-groups replace the o- and p-hydrogen atoms referred to hydroxyl, and with reference to one another, in the m-position:

$$C_6H_5OH \begin{cases} \longrightarrow C_6H_4\{[1]OH,[2]NO_2 \longrightarrow C_6H_3\{[1]OH,[2]NO_2,[6]NO_2 \\ \longrightarrow C_6H_4\{[1]OH,[4]NO_2 \longrightarrow C_6H_3\{[1]OH,[2]NO_2,[4]NO_2 \end{cases} \longrightarrow C_6H_2\{[1]OH,[2]NO_2,[4]NO_2,[6]NO_2$$

While the colourless or faint-yellow free nitro-phenols are undoubtedly true phenols, the intensely red or yellow salts of the nitro-phenols, as in the aliphatic nitro-compounds, are probably derivable from a hypothetical nitrous acid of the structure $O{=}C_6H_4{=}N\langle^{O}_{OH'}$ which is designated as an aci-nitro-phenol form (B. **39**, 1084). Considerable support is given to this view by the observation that the ethers of the nitro-phenols exist in two isomeric series (B. **39**, 1073). Besides the colourless normal nitro-phenol ethers, the halogen alkyls, acting upon the silver salts of the nitro-phenols, produce very unstable ethers of a deep-red colour. These pass spontaneously into the colourless isomeric ethers, and are quickly saponified with water alone, with regeneration of the nitro-phenols. These unstable ethers correspond to the strongly coloured nitro-phenol salts, and probably also possess a quinoid structure: $O{=}C_6H_4{=}N\langle^{O}_{OCH_3}$. Of the m-nitro-phenols only the normal, colourless ethers have hitherto been obtained, and this corresponds to the absence of m-quinones.

Mononitro-phenols $NO_2.C_6H_4.OH$.—Dilute nitric acid converts phenol into o- and p- mononitro-phenol (in the cold it is chiefly the p-compound which is formed). At −67°, with the use of the electric spark, there is five times as much of the p-body as at −40° (B. **26**, R. 362).

The o and p-compounds are separated by distillation with steam, in which the p-compound is not volatile. Phenol in presence of sulphuric acid is also nitrated by nitrogen dioxide (B. **24**, R. 722). o-Nitro-phenol is also obtained, together with a little of the para-body, from nitro-benzol on heating with dry potash; or from the product of metallic sodium and nitro-benzol under a current of air.

o- and p-Nitro-phenols are also obtained by heating the corresponding chloro- and bromo-nitro-benzols with caustic potash to 120°, whereas m-bromo-nitro-benzol does not react under similar circumstances. Ortho- and para-nitro-phenols are likewise produced from the corresponding nitranilines by heating with alkalies. m-Nitro-phenol is formed from m-nitraniline (from ordinary dinitro-benzol) by boiling the diazo-compound with dilute sulphuric acid. p-Nitro-phenol has also been obtained synthetically from nitro-malonic aldehyde with acetone.

It is obtained from p-nitroso-phenol by oxidation with nitric acid (C. 1903, I. 144). o-Nitro-phenol is formed, besides polynitro-phenols, on the nitrogenation of benzene in the presence of mercury nitrate:

o-Nitro-phenol, m.p. 45°, b.p. 214°; methyl ether, m.p. +9°, b.p. 265°
m-Nitro-phenol, ,, 96°, .. methyl ether, ,, 38°, ,, 254°
p-Nitro-phenol, ,, 114°, .. methyl ether, ,, 48°, ,, 260°.

o- and m-Nitro-phenols form yellow crystals; the latter is rather soluble in water. The o-body has a peculiar odour and sweet taste. Its sodium salt forms dark-red prisms.

p-Nitro-phenol crystallises from hot water in long, colourless needles. The potassium salt crystallises in yellow needles with two molecules of water.

With HgO or mercuric nitrate the nitro-phenols yield, in the first instance, the mercury salts of the phenols, $(NO_2C_6H_4O)_2Hg$, which pass into **mercuri-nitro-phenols,** the Hg wandering to the nucleus. These easily form the intensely coloured **mercuric anhydrides,** probably derivable from the formula o: $C_6H_3\langle^{NO}_{Hg}\rangle O$ (B. **39**, 1105). By bromination, the p-nitro-phenol passes into [1, OH, 2, 6, 4]-**dibromo-p-nitro-phenol,** m.p. 141°; [4, 6]-**dibromo-2-nitro-phenol,** m.p. 117°, is formed from 2, 4, 6-tribromo-phenol with ethyl nitrite in alcoholic solution.

Dinitro-phenols $(NO_2)_2C_6H_3OH$.—α- or [1 OH, 2, 4]-**Dinitro-phenol,** melting at 114°, and β- or [1 OH, 2, 6]-**dinitro-phenol,** melting at 64°, are produced in the nitration of phenol and of *o-nitro-phenol.* The α-compound can also be obtained from p-nitro-phenol, as well as from m-dinitro-benzol, by means of alkaline potassium ferricyanide. The *α-methyl ether* melts at 86°. It is transformed into [1 NH_2, 2, 4]-dinitraniline by heating with ammonia.

The nitration of [1, 3]-nitro-phenol produces three isomeric *dinitro-phenols*, melting at 104°, 134°, and 141°. Further nitration produces *trinitro-phenols* and *trinitro-resorcin.*

Sym. **dinitro-phenelol** $C_6H_5O[1]C_6H_4[3, 5](NO_2)_2$, m.p. 96°, is obtained by the action of sodium ethylate upon trinitro-benzol (C. 1906, I. 833).

Trinitro-phenols.—Picric acid $C_6H_2(NO_2)_3.OH$, melting at 122°, is obtained by the nitration of phenol, of [1, 2]- and [1, 4]-nitro-phenol,

and of the two dinitro-phenols; also, by the oxidation of symmetrical trinitro-benzol with potassium ferricyanide. It is therefore [1 OH, 2, 4, 6]-trinitro-phenol.

Picric acid is produced in the action of concentrated nitric acid upon various organic substances, like indigo, aniline, resins, silk, leather, and wool.

History.—Woulfe found, in 1711, that nitric acid acting on indigo produced a liquid which coloured silk yellow. Welter, in 1799, first prepared pure picric acid by nitrating silk. It was called Welter's *bitter*. Liebig called it *carbon-nitric acid, carbazotic acid.* Dumas analysed it and called it *picric acid,* from πικρός, bitter. Laurent, in 1842, discovered it to be a derivative of phenol.

Properties.—Picric acid crystallises from hot water and alcohol, in yellow flakes or prisms which possess a very bitter taste. It dissolves in 160 parts of cold water, and rather readily in hot water. Its solution imparts a beautiful yellow colour to silk and wool. It sublimes undecomposed when carefully heated.

Behaviour.—With many hydrocarbons, like benzene, naphthalene, and anthracene, picric acid forms beautiful crystalline derivatives, well adapted for the recognition and separation of the higher aromatic hydrocarbons.

The action of PCl_5 upon picric acid produces picryl chloride. On heating barium picrate in an aqueous solution of bleaching lime, chloropicrin is formed (Vol. I.).

Prussic acid is produced on boiling a solution of barium picrate with baryta water. Picric acid is converted by potassium cyanide into the potassium salt of **isopurpuric** or **picro-cyaminic acid** $C_8H_4N_5O_6K$. It crystallises in brown flakes with green-gold lustre, and formerly appeared in commerce under the name *Grênat soluble.* It is no longer used. Isopurpuric acid, liberated from its potassium salt by phosphoric acid, and of a deep-violet colour, possesses, according to its decomposition products, the constitution C_6[2, 6](CN)$_2$[1, 3](NO$_2$)$_2$[4, 5](OH)(NHOH). A behaviour towards KCN resembling that of picric acid is also shown by o, p- and o, o-dinitro-phenols and other polynitro-phenol derivatives (B. **87,** 1843, 4388; **88,** 3538, 3938).

Salts and Ethers.—The *potassium salt,* $C_6H_2(NO_2)_3.OK$, crystallises in yellow needles, soluble in 260 parts of water at 15°. The *sodium salt* is soluble in 10 parts water at 15°, and is separated from its solution by sodium carbonate. The *ammonium salt* consists of beautiful large needles, and is applied in explosive mixtures. All the picrates explode very violently when heated or struck.

The *methyl ether* of picric acid is produced in the nitration of anisol. It melts at 65°. The *ethyl ether* melts at 78°.

β-Trinitro-phenol, melting at 96°, and **γ-trinitro-phenol,** m.p. 117°, have been obtained from the dinitro-phenols resulting from the nitration of m-nitro-phenol.

Tetranitro-phenol, m.p. 130°, consists of golden-yellow needles. It is produced in the oxidation of diquinoyl-trioxime (*q.v.*). It is very explosive (B. **80,** 184).

Tetranitro-anisol, m.p. 154° (C. 1904, II. 205).

Nitro-cresols.—**o-Nitro-p-cresol** NO$_2$[2]CH$_3$[4]C$_6$H$_3$OH, m.p. 77°, and **p-nitro-o-cresol,** m.p. 118°, are prepared pure from the corre-

sponding nitro-toluidins. The former is also easily obtained by nitrogenation of p-cresol carbonate, and saponification of the resultant compound (C. 1909, I. 965). By the action of fuming sulphuric acid it is split up with formation of acetyl-acrylic acid (B. **42,** 577). By further nitrogenation of the methyl ethers of o-nitro-p-cresol and p-nitro-o-cresol we obtain o-dinitro-compounds (B. **34,** 2238). Nitrogenation of o- and p-cresol easily yields dinitro-derivatives (B. **15,** 1858). Of these, the [2, 6]-**dinitro-p-cresol,** m.p. 84°, has been used as an orange dye in the form of its sodium salt, called *Victoria orange,* or *saffron substitute.* **Dinitro-o-cresol** is used as an insecticide in the form of salt-solutions, more especially against caterpillars, under the name of Antinonnin (B. **27,** R. 316). Nitrogenation of m-cresol yields a **trinitro-cresol** $(NO_2)_3C_6H(CH_3)OH$, m.p. 106°, also formed from nitrococcus acid, and by nitrating thymol (C. 1901, II. 411). **Tetranitro-m-cresol,** m.p. 175° (C. 1908, I. 724). **Nitro-xylenols,** see B. **42,** 2917; C. 1904, II. 1213.

Haloid Nitro-phenols.—Numerous representatives of this class have been obtained by the action of the halogens upon the nitro-phenols, or by the nitration of the haloid phenols.

It is interesting to note that **p-nitro-o-iodanisol** $C_6H_3[4]NO_2[2]I[1]OCH_3$ has been prepared both in the nitration of o- as well as in that of p-iodanisol. In the latter case, therefore, a migration, or wandering, of the iodine atom in the nucleus has occurred (B. **29,** 997).

Nitroso-compounds of the Phenols.

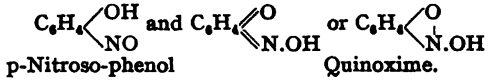
The nitroso-phenols are made: (1) by the action of nitrous acid upon phenols (Baeyer, B. **7,** 964), when the monohydric phenols yield only mononitroso-compounds; whereas dinitroso-derivatives are obtained from the dihydric meta-dioxy-benzols, like resorcin.

(*a*) Nitrous acid, from alkali nitrite and dilute sulphuric acid or acetic acid, is allowed to act upon the phenols (B. **7,** 967; **8,** 614); (*b*) by means of the nitrites of heavy metals, which are decomposed by the phenols themselves (B. **16,** 3080); (*c*) from nitrosyl-sulphuric acid $HO.SO_2.NO$ and phenols (A. **188,** 353; B. **21,** 429); (*d*) from amyl nitrite and sodium phenolates (B. **17,** 803).

(2) Upon boiling p-nitroso-alkylamines, like nitroso-dimethyl-aniline (I. 163; II. 94) with alkalies:

$$NO[4]C_6H_4[1]N(CH_3)_2 + NaOH = NO[4]C_6H_4[1]OK + HN(CH_3)_2.$$

(3) By the action of HCl hydroxylamine upon quinones in aqueous or alcoholic solution. Free hydroxylamine reduces the quinones to hydroquinones (B. **17,** 2061). This method favours the idea that the nitroso-phenols are quinone-monoximes (Goldschmidt, B. **17,** 801). Hence, three constitutional formulas have been brought forward for p-nitroso-phenol or quinone-monoxime (Quinones, *q.v.*):



p-Nitroso-phenol Quinoxime.

o-Nitroso-phenol $HO.C_6H_4[2]NO$: as aniline is oxidised to nitroso-benzol, so o-anisidin is oxidised by Caro's acid to o-nitroso-anisol

$CH_3OC_6H_4$[2]MO, m.p. 103°; on saponification with bisulphate, this yields the o-nitroso-phenol, the Na salt of which forms deep-red flakes (B. **35,** 3036).

p-Nitroso-phenol, quinone-monoxime, crystallises from hot water in colourless, delicate needles, which readily brown on exposure, and from ether it separates in large greenish-brown flakes; also by the action of nitroso-benzol and NaHO (B. **38,** 1954). It is soluble in water, alcohol, and ether, and imparts to them a bright-green colour. When heated, it melts with decomposition, and deflagrates at 110°–120°. The *sodium salt* crystallises in red needles, containing two molecules of water of crystallisation.

The methods of producing nitroso-phenol from phenol with nitrous acid, and from nitroso-dialkyl-anilines, argue for the nitroso-formula of the nitroso-phenols; as does their oxidation to p-nitro-phenol with nitric acid or with an alkaline potassium ferricyanide solution.

The quinoxime formula is supported by their formation from quinone with hydroxylamine hydrochloride, and the conversion into quinodioxime, as well as by the formation of hypochlorous esters $C_6H_4(O).NOCl$ when acted upon by bleaching-lime (B. **19,** 280). Further, by the behaviour of the related nitroso-naphthols (*q.v.*), and finally the feeble basic character of the nitroso-phenols (B. **18,** 3198; **19,** 280). Methylation of nitroso-phenol yields, not nitroso-anisol, but quinone-methoxime $O:C_6H_4:NOCH_3$, m.p. 83°; **p-nitroso-anisol** $CH_3OC_6H_4$[4]NO, m.p. 23°, from p-anisidin, by oxidation with monopersulphonic acid (Caro's acid), or from p-anisol-hydroxylamine with ferric chloride (B. **37,** 44). By dilute H_2SO_4 it is easily saponified into p-nitroso-phenol (B. **35,** 3034).

Possibly the free nitroso-phenols have a quinone-oxime formula, while the salts are derivable from the nitroso-phenol formula (cp. B. **32,** 3101).

The nitroso-phenols can be changed to nitroso-anilines. Hydrochloric acid converts nitroso-phenol into dichloramido-phenol. With nitrous acid and with hydroxylamine it yields p-diazo-phenol:

$$HOC_6H_4NO \xrightarrow{NH_2OH} (HOC_6H_4N_2OH) \longrightarrow O:C_6H_4:N_2.$$

In a similar manner it forms azo-compounds with the amines. Phenyl-hydrazin reduces it very readily to amido-phenol (B. **29,** R. 294). On adding a little concentrated sulphuric acid to a mixture of nitroso-phenol and phenol, we obtain a dark-red coloration, which changes to dark blue upon adding caustic potash.

Nitroso-m-cresol, m.p. 155° (B. **21,** 729; C. 1900, I. 120).

Nitroso-o-cresol, from o-cresol and toluquinone (*q.v.*) (B. **21,** 729), m.p. 134°.

Nitroso-thymol melts at 160° (B. **17,** 2061; A. **310,** 89).

AMIDO-PHENOLS.

These result from the reduction of nitro- and nitroso-phenols, or the oxy-azo-compounds (B. **38,** 2752). In the case of poly-nitrated phenols, ammonium sulphide occasions but a partial reduction; tin and hydrochloric acid, however, effect a complete reduction of the

nitro-groups. For special methods of formation, see m- and p-amido-phenol.

Behaviour.—The free amido-phenols decompose quite easily, especially in moist air on exposure to light.

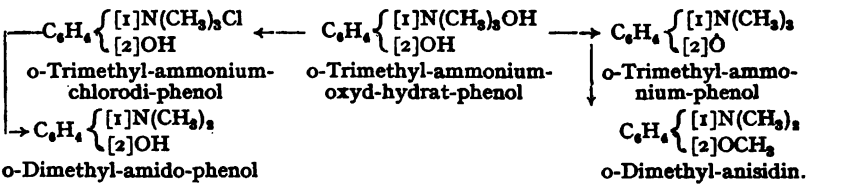
The amido-group considerably diminishes the acid character of the phenols. This class of derivatives no longer forms salts with alkalies, and only yields such compounds with the acids.

Like the o-phenylene-diamines, the o-amido-phenols form heterocyclic derivatives with ease. These are anhydro-bases; the *benzoxazoles*, corresponding to the *benzimide-azoles*, are similar bodies obtained from the o-amido-thio-phenols.

o-Amido-phenol $NH_2[2]C_6H_4[1]OH$, m.p. 170°, dissolves with difficulty in water. **o-Anisidin** $NH_2[2]C_6H_4[1]OCH_3$, b.p. 218°.

o-Imido-diphenyl oxide, phenoxazin $O\langle{}^{C_6H_4}_{C_6H_4}\rangle NH$ will be described together with thio-diphenyl-amine, hydro-phenazin, and phenazin under the heterocyclic compounds (cp. also pyro-catechol).

Methylation of the Amido-group of o-Amido-phenol (B. **23**, 246).—When o-amido-phenol in methyl alcohol is treated with methyl iodide and caustic potash, and later with hydrogen iodide, there results the iodide of an ammonium base, which moist silver oxide changes to the ammonium hydroxide. The latter loses water at 105°, and changes to a cyclic ammonium derivative similar to betaïn: **o-trimethyl-ammonium-phenol,** which, heated to higher temperatures, rearranges itself into **o-dimethyl-anisidine.** The hydrochloride of the ammonium base breaks down upon distillation into methyl chloride and **o-dimethyl-amido-phenol,** m.p. 45°:



o-Methyl-amido-phenol $CH_3NH[2]C_6H_4[1]OH$, from **o-methyl-anisidin** $C_6H_4(NHCH_3)OCH_3$, with HCl. Its sulphate, mixed with hydroquinone, is sold as a photographic developer under the name " ortol " (B. **82**, 3514); see also Metol (C. 1903, I. 1129).

o-Oxethyl-anisidin $HO.CH_2CH_2.NH[2]C_6H_4[1]OCH_3$, from o-anisidin and ethylene-chloro-hydrin, b.p. 305°.

o-Formyl-amido-phenol $CHO.NHC_6H_4OH$, m.p. 129°, from o-amido-phenol with formic acid. Also, besides *anthranile*, from *o-amido-benzaldehyde* by oxidation with Caro's acid, probably by transposition of o-hydroxylamine-benzaldehyde $CHO.C_6H_4.NHOH$. On heating to 160°–170° it passes into *benzoxazol* (B. **36**, 2042). For acylated o-amido-phenols, see C. 1907, I. 806.

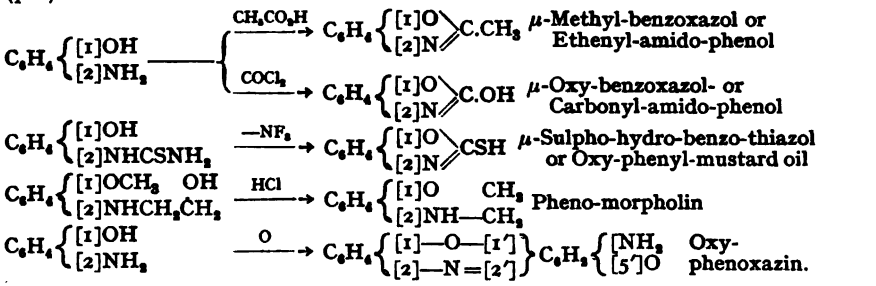
o-Oxy-phenyl-urethane $COOC_2H_5.NH[2]C_6H_4[1]OH$, m.p. 86°, is formed by the reduction of o-nitro-phenyl-ethyl carbonate by transposition of the first product, viz. **o-amido-phenyl-ethyl carbonate** $NH_2[2]C_6H_4[1]O.COOC_2H_5$. **Chlorohydrate,** m.p. 151° (C. 1900, I. 413; 1904, II. 94, 695). This transformation of the O-acyl compounds of

the o-amido-phenols into the isomeric N-acyl compounds is quite a general reaction. It is so straightforward that the O-acyl-o-amido-phenols can usually not be obtained (cp. the similar transformations in the o-oxy-benzylamines and o-amido-benzyl alcohols, A. **332**, 159; **364**, 147).

o-Oxy-phenyl-urea $NH_2CONH[2]C_6H_4[1]OH$, m.p. 154°. **o-Oxy-phenyl-thiurea** $NH_2CSNH[2]C_6H_4[1]OH$, m.p. 161°.

o-Oxy-diphenyl-amine $OH[2]C_6H_4[1]NHC_6H_5$, m.p. 70°, produced by the action of acetyl and benzoyl peroxide upon diphenyl-amine (B. **42**, 4003).

The Condensations of the o-Amido-phenols.—(1) **Benzoxazoles** result by the union of o-amido-phenol with carboxylic acids; thus, with acetic acid the product is *μ-methyl-benzoxazole.* (2) With phosgene it is *μ-oxy-benzoxazole*, or *carbonyl-amido-phenol.* The latter body is also produced upon heating o-oxy-phenyl-urea (see above). (3) On heating, o-oxy-phenyl-thiurea yields *o-oxy-phenyl-mustard oil.* (4) o-Oxy-ethyl-anisidine, when heated with hydrochloric acid, becomes *pheno-morpholine* (*q.v.*). (5) Oxidants convert o-amido-phenol into *oxy-phenoxazin* (*q.v.*). o-Amido-phenol and pyro-catechol condense to phenoxazin (*q.v.*).



m-Amido-phenol, m.p. 122°, is obtained from m-nitro-phenol (B. **11**, 2101), from the oxamic acid derivative of m-phenylene-diamine (B. **28**, R. 30); by melting up metalinic acid with caustic soda (B. **32**, 2112), and by heating resorcin to 200° with ammonium chloride and aqueous ammonia.

Monoalkyl-m-amido-phenols (B. **27**, R. 953; **22**, R. 622).—**Dimethyl-m-amido-phenol** melts at 87°; **diethyl-m-amido-phenol** boils about 280°. m-Amido-phenol and its alkyl derivatives are employed in the preparation of *rhodamine dyes.*

Consult B. **29**, 501, for the action of phosgene upon the alkyl m-amido-phenols. **Trimethyl-m-amido-phenol** $C_6H_4[1]OH[3]N(CH_3)_3OH$, see B. **29**, 1533.

p-Amido-phenol melts at 184° with decomposition, and sublimes. It results (1) from p-nitro-phenol; (2) from β-phenyl-hydroxylamine; (3) by the action of the electric current upon nitro-benzol in strong sulphuric acid solution; its formation here is due to the rearrangement of the β-phenyl-hydroxylamine produced at first; (4) from [5]-amido-salicylic acid by elimination of CO_2; (5) by heating p-chloro-phenol with ammonia in the presence of copper (C. 1909, I. 600). By oxidation with silver oxide it yields quinone mono-imine.

It is oxidised to quinone by chromic acid, or by PbO_2 and sulphuric

acid. Bleaching-lime converts it, as well as its substitution products, into quinone chlorimides. p-Amido-phenol acts the same, and just as readily, as phenyl-hydrazin upon aldehydes and ketones in dilute acetic acid (B. **27**, 3005). Ethers of p-amido-phenetol are produced by reduction of p-nitro-phenol ether (B. **34**, 1935), as well as by the transposition of β-phenyl-hydroxylamine with alcoholic H_2SO_4 (B. **33**, 3602). Methyl ether, p-anisidin, m.p. 56°, b.p. 246°.

p-Amido-phenetol, p-phenetidine $NH_2[4]C_6H_4[1]OC_2H_5$ is the ethyl ether. It boils at 242°. Boiling glacial acetic acid converts it into **p-acetamido-phenetol** $C_6H_4\langle^{NH.CO.CH_3}_{O.C_2H_5}$, **phenacetin,** melting at 135°, which has been applied as an antipyretic.

The splitting up of phenacetin by 80 to 90 per cent. sulphuric acid into acetic ether and p-amido-phenol is worthy of note (A. **309**, 233). On prolonged boiling with excess of acetic anhydride (B. **31**, 2788), phenacetin is converted into *diacetyl-phenetidin* $(CH_3CO)_2NC_6H_4OC_2H_5$, m.p. 54°, b.p.$_{12}$ 182°, which has an action similar to phenacetin, as has also *p-ethoxy-phenyl-succinimide*, **pyrantin** $(CH_2CO)_2NC_6H_4OC_2H_5$, melting at 155°, which, it is claimed, does not have the unpleasant action or after-effects peculiar to phenacetin (B. **29**, 84). **p-Phenetol-carbamide,** " dulcin," $NH_2CO.NH[4]C_6H_4[1]OC_2H_5$ (B. **28**, R. 78, 83), has a very sweet taste.

m-Oxy-diphenyl-amine $C_6H_5NH[3]C_6H_4[1]OH$, melting at 82° and boiling at 340°, and **p-oxy-diphenyl-amine,** melting at 70° and boiling at 330°, are formed on heating resorcin and hydroquinone with aniline and zinc chloride (B. **22**, 2909). For homologues, see C. 1902, I. 578. p_2-Dioxy-diphenyl-amine $NH(C_6H_4[4]OH)_2$, m.p. 174°, is obtained from hydroquinone by heating with ammonia or with p-amido-phenol (B. **32**, 689). The oxy-diphenyl-amines are closely related to the indo-phenol dyes (see Quinones). p_2-Amido-oxy-diphenyl-amine $NH_2C_6H_4NHC_6H_4OH$, m.p. 166°, is formed by the reduction of the corresponding nitro-compound (B. **42**, 1080) or by oxidation of a mixture of p-phenylene-diamine and phenol with hypochlorite in the presence of copper salts (C. 1909, I. 115). The solution of p-amido-p-oxy-diphenyl-amine in alkalies soon acquires a blue colour with the formation of indamine. **p_2-dimethyl-amido-oxy-diphenyl-amine** $N(CH_3)_2C_6H_4NHC_6H_4OH$, m.p. 161°, see B. **35**, 3085.

Diamido-phenols. — **[2,4]-Diamido-phenol** $(NH_2)_2[2,4]C_6H_3[1]OH$ is obtained from [2, 4]-dinitro-phenol, and by the electrolytic reduction of m-dinitro-benzol or m-nitro-aniline in sulphuric acid (B. **26**, 1848). The free base is very unstable, and its salts have been used as developers in photography under the name **amidol.** 4, 5- and 2, 5-Diamido-phenols are formed from the nitro-amido-phenols obtained by the action of H_2SO_4 upon the o- and p-nitro-diazo-imides (B. **30**, 2096; **31**, 2403). **m-Anilido-p-phenitidin** $C_6H_5NH[3]C_6H_3\{^{[1]OC_2H_5}_{[4]NH_2}$; see Hydrazin phenols for its formation.

Picramic acid, [2]-amido-[3, 4]-dinitro-phenol $C_6H_2(NH_2).(NO_2)_2.OH$, is obtained by the reduction of picric acid with alcoholic Am_4SH or with sodium hydrosulphite. (For further dinitro-p-amido-phenols, see B. **38**, 1593.) It forms red needles, which melt at 165°.

[2, 4, 6]-Triamido-phenol $C_6H_2(NH_2)_3.OH$ is obtained from picric

acid by the action of phosphorus iodide, or by tin and hydrochloric acid (B. **16**, 2400). When set free from its salts, it decomposes very quickly. Its salts, with three equivalents of acids, crystallise well. The HI-salt, $C_6H_3O(NH_2)_3.3HI$, crystallises in colourless needles. These salts colour water which is faintly alkaline, and even spring water, a beautiful blue. If ferric chloride be added to the solution of the hydrochloride, it will become deep blue in colour, and brown-blue needles with metallic lustre will separate; they are *HCl-amido-di-imido-phenol*, or diamido-quinone-imine, which dissolves in water with a beautiful blue colour.

An isomeric triamido-phenol has been prepared by reducing di-quinoyl-trioxime (B. **30**, 183).

[2, 3, 4, 5]-Tetramido-anisol $(NH_2)_4C_6HOCH_3$ (B. **25**, 282).

Diazo-phenols.—*Phenol-diazo-chlorides* $HO.C_6H_4N_2Cl$ result from the action of nitrous acid upon the hydrochlorides of the amido-phenols.

The diazonium polyhaloids, nitrates, and sulphonates, with weak acids, like acetic acid and carbonic acid, form, by the replacement of a halogen atom, a nitroyl or a sulphoxyl in the o- or p-position by hydroxyl-substituted diazo-phenols (B. **36**, 2069; **39**, 79; C. 1903, I. 393; 1907, II. 1785). The free diazo-hydrates of the o- and p-amido-phenols anhydrate themselves, the yellow, so-called quinone diazides being generated, probably by a transposition into the quinoid form (cp. Vol. I., Diazo-methane, and B. **35**, 888):

$$\begin{matrix} N \\ \diagup \\ N \end{matrix}\!\!>\!C_6H_4{=}O \qquad \begin{matrix} N \\ \diagup \\ N \end{matrix}\!\!>\!C_6H_2Cl_2{=}O \qquad \begin{matrix} N \\ \diagup \\ N \end{matrix}\!\!>\!C_6H_2(NO_2){=}O.$$

p-Diazo-phenol cyanide $HO[4]C_6H_4N_2.CN$, from the action of potassium cyanide on the chloride, consists of yellow needles. Caustic potash saponifies it to the potassium salt of **diazo-phenol-carboxylic acid** $HO.C_6H_4N_2COOH$.

Dibromo-diazo-phenol $Br_2[4, 6]C_6H_2(:O)(:N_2)[1, 2]$, orange prisms, m.p. 130° with decomposition (B. **39**, 4248).

Dibromo-phenol-diazo-sulphonic acid $C_6H_2Br_2(OH)N_2SO_3H+2H_2O$ can be isolated from its potassium salt produced from the interaction of potassium sulphite and dibromo-phenol-diazo-chloride.

p-Phenol-diazo-mercaptan hydrosulphide $C_6H_4(OH).N_2SH.SH_2$, from the action of hydrogen sulphide upon diazo-phenol solutions, consists of red needles melting at 75° with decomposition (B. **28**, 3250).

p-Oxy-diazo-benzol-imide $OH[1]C_6H_4[4]N_3$, m.p. about 20°, explodes at 150°. From p-amido-phenol with nitrous acid. The potassium compound exists in two forms, one colourless, the other blue, easily convertible into each other. Both yield the same benzoyl compound, of m.p. 81°, which is also obtained from benzoyl-p-amido-phenol with nitrous acid (C. 1907, II. 247).

Azoxy-phenols.—p-Oxy-azoxy-benzol $C_6H_5(N_2O)C_6H_4[4]OH$, m.p. 156°, is obtained by the combination of p-nitroso-phenol with β-phenyl-hydroxylamine and elimination of water; it also forms on the action of sodium hydroxide upon nitroso-benzol at 100°, which also produces two isomeric o-oxy-azoxy-benzols, m.p. 76° and 108° respectively. Oxidation with permanganate disintegrates the oxy-azoxy-benzols to **potassium iso-diazo-benzol**:

$$C_6H_5(N_2O)C_6H_4OH \longrightarrow C_6H_5N_2OK$$

(B. **35**, 1614).

Azo-phenols, Oxy-azo-benzols.—*Formation*:—(1) From diazo-salts and monohydric phenols, m-dioxy-benzols, m-amido-phenols, and m-phenol-sulphonic acids:

$$C_6H_5N_2.NO_3+C_6H_5OH = C_6H_5N:N[1]C_6H_4[4]OH.$$

The solution of the diazo-salt is allowed to run into the alkaline phenol solution while cooling and stirring. Phenol-diazo-benzol is produced, together with phenol-azo-benzol.

As with the amido-azo-compounds, the entering diazo-group arranges itself in the phenols in the p-position, and when this is already occupied it takes the o-position with reference to the hydroxyl group (B. **17**, 1876; **21**, R. 814).

Intermediate products have been sometimes isolated in this reaction in the form of the so-called o-azo-compounds (diazo-oxy-benzols), corresponding to the diazo-amido-compounds, which, however, transpose themselves with even greater ease into the isomeric oxy-azo-compounds (B. **41**, 4016, 4304):

$$C_6H_5O.N:N.C_6H_5 \longrightarrow C_6H_5N:N.C_6H_4OH.$$

(2) By heating the diazo-amido-benzols with monohydric phenols, and also with resorcin (B. **20**, 372, 904, 1577):

$$C_6H_5.N_2.NH.C_6H_5+C_6H_5.OH = C_6H_5.N_2.C_6H_4.OH+C_6H_5.NH_2.$$

(3) By the molecular rearrangement induced by heating azoxy-benzols with sulphuric acid (B. **14**, 2617):

$$\begin{matrix}C_6H_5N\\C_6H_5N\end{matrix}\!\!>\!O \longrightarrow C_6H_5N_2.C_6H_4.OH$$

Azoxy-benzol — Oxy-azo-benzol.

(4) By reduction of the nitro-phenols in alcoholic potassium hydroxide solution.

(5) By the action of anilines upon nitroso-phenols.

(6) From amido-azo-benzols and from azo-benzol-sulphonic acids.

Constitution.—The oxy-azo-compounds, containing hydroxyl in the ortho-position to the azo-group, are probably quinone-hydrazones:

$$C_6H_4\begin{cases}OH\\N:NC_6H_5\end{cases} \qquad C_6H_4\begin{cases}:O\\:NNHC_6H_5\end{cases} \text{ or } C_6H_4\begin{cases}O\\NNHC_6H_5\end{cases}$$

Oxy-azo-benzol — Quinone-phenyl-hydrazone.

Quinone-phenyl-hydrazone itself is not obtained by condensation of benzo-quinone, since the quinone is reduced by phenyl-hydrazin, but the monophenyl-hydrazins of quinone have been obtained with o-nitro- and o-, p-dinitro-phenyl-hydrazin. The latter have proved themselves to be identical with the nitro-oxy-azo-compounds obtained by coupling diazotated o-nitro- and o-, p-dinitro-aniline with phenol (A. **357**, 171; see also Naphtho-quinone-hydrazones):

$$C_6H_4\begin{cases}[1]O\\[4]O\end{cases} \xrightarrow{H_2N.NHC_6H_4NO_2} C_6H_4\begin{cases}[1]N:NC_6H_4NO_2\\[4]OH\end{cases} \xleftarrow{ClN:NC_6H_4NO_2} C_6H_5OH.$$

Unsym. acetyl- and benzoyl-phenyl-hydrazin also yield n-acylated quinone-phenyl-hydrazones with quinone, and these, on saponification, pass into p-oxy-azo-benzol. They are isomeric with the o-acyl-oxy-

azo-benzols obtained by acetylation or benzoylation of oxy-azo-benzol (C. 1900, I. 30).

Of special importance for deciding the question of the constitution of the oxy-azo-compounds is the observation that the N-acylated p-quinone-phenyl-hydrazones are transposed with great facility into the isomeric O-acylated oxy-azo-benzols (B. **40,** 1432) :

$$C_6H_4\begin{cases}[1]:N.N(COCH_3)C_6H_5\\ [4]:O\end{cases} \longrightarrow C_6H_4\begin{cases}[1]N:NC_6H_5\\ [4]O(COCH_3)\end{cases}.$$

The tendency to pass into true azo-compounds is so great among the o-quinones that the isomeric N-acylated o-quinone-phenyl-hydrazones have not been obtained at all up to the present time (B. **40,** 2154 ; A. **359,** 353 ; but cp. C. 1909, I. 1093). On account of this easy conversion of derivatives of quinone-phenyl-hydrazone into those of oxy-azo-benzol, we are justified in regarding the free o- and p-oxy-azo-compounds as true azo-compounds. This is in agreement with the fact that the m-oxy-azo-benzol (see below), which, on account of the non-existence of m-quinones, cannot be formulated as a quinone-phenyl-hydrazone, closely corresponds in its behaviour to o- and p-oxy-azo-benzol (B. **36,** 4118). With phenyl cyanate, o- and p-oxy-azo-benzol combine to O-carbanilido-derivatives, $C_6H_4\begin{cases}N:NC_6H_5\\ OCONHC_6H_5\end{cases}$ (B. **38,** 1098). The total or partial insolubility of oxy-azo-compounds in alkalies, which was regarded as a special argument in favour of their quinone structure, finds its analogy in the similar behaviour of the phenyl-hydrazones of the o-phenol-aldehydes and ketones (B. **35,** 4100 ; C. 108, II. 306).

p-Oxy-azo-benzol, benzol-p-azo-phenol $C_6H_5N{=}N[1]C_6H_4[4]OH$, m.p. 148°, crystallises in orange-yellow needles. It is produced by the methods mentioned in connection with oxy-azo-derivatives ; treated with phosphorus pentachloride, and then with water, it is converted into the phosphoric ester $PO(OC_6H_4N_2C_6H_5)_3$, m.p. 148° (B. **24,** 365 ; cp. **35,** 1622). **Benzol-p-azo-phenetol,** m.p. 77° (B. **25,** 994). **p-Azo-phenol** $HO[4]C_6H_4[1]N_2[1]C_6H_4[4]OH$, m.p. 204°, consists of light-brown crystals. It is produced :

(1) By fusing p-nitro- and nitroso-phenol with caustic alkali.
(2) By the pairing of diazo-benzol nitrate with phenol.
(3) From p-oxy-azo-benzol-sulphonic acid (B. **15,** 3037).

o-Oxy-azo-benzol, m.p. 83°, is volatile with water vapour, therein contrasting with the p-derivative ; it is formed beside the p-oxy-azo-benzol in small quantities from benzol-diazonium salts with phenol (B. **33,** 3189) ; also by transposition of azoxy-benzol (C. 1903, I. 324, 1082) ; and partly by the action of NaHO upon nitroso-benzol (B. **33,** 1939). Its methyl ether, **benzol-azo-o-anisol,** m.p. 41°, obtained synthetically from o-anisidin and nitroso-benzol, also yields with Al_2Cl_6 the o-oxy-azo-benzol (B. **33,** 3190).

m-Oxy-azo-benzol, m.p. 114°–117°, canary-yellow crystals, is formed by the coupling of o-amido-phenetol with diazo-benzol chloride, with splitting off of the amido-group, and saponification of the resulting **benzol-azo-m-phenetol,** m.p. 64°, with Al_2Cl_6 (B. **36,** 4102) :

$$C_6H_3\begin{cases}[1]OC_2H_5\\ [2]NH_2\end{cases} \longrightarrow C_6H_3\begin{cases}[1]OC_2H_5\\ [2]NH_2\\ [5]N:NC_6H_5\end{cases} \longrightarrow C_6H_3\begin{cases}[1]OC_2H_5\\ [5]N:NC_6H_5\end{cases} \longrightarrow C_6H_3\begin{cases}[1]OH\\ [5]N:NC_6H_5\end{cases}.$$

mm'-Dioxy-azo-benzol, *m-azo-phenol,* m.p. 205°, is formed by fusing m-nitro-phenol with caustic potash (B. **89,** 303). It has also been prepared from m-azo-aniline, by means of diazo-compounds, and from m-nitro-phenol by electrolytic reduction (C. 1902, II. 1182; 1903, I. 1221).

Concerning azo- and diazo-compounds of cresol, see B. **17,** 351.

The sulpho-acids of the oxy-azo-benzols are *dyes—e.g.* **p-sulpho-benzol-p-azo-phenol** $SO_3H[4]C_6H_4[1]N=N[2]C_6H_4[4]OH$, from p-oxy-azo-benzol and sulphuric acid, and from p-diazo-benzol-sulphonic acid by means of sodium phenate, is the *tropæoline yellow* of commerce (B. **11,** 2192). Also compare resorcin.

Phenol-2, 4-dis-azo-benzol $OH[1]C_6H_3[2, 4](N : NC_6H_5)_2$, m.p. 123° (C. 1904, II. 96), and **phenol-2, 4, 6-tris-azo-benzol** $OH[1]C_6H_2[2, 4, 6](N : NC_6H_5)_3$, m.p. 215°, are formed by coupling phenol with 2, or 3, molecules of diazo-benzol chloride in alkaline solution. Tin and HCl reduce phenol-tris-azo-benzol to 2, 4, 6-tri-amido-phenol (*J. pr. Ch.* 2, **78,** 384).

Hydrazo-phenols.

m-Oxy-hydrazo-benzol $OH[1]C_6H_4[3]NH.NHC_6H_5$, colourless needles, m.p. 126°, is obtained by reduction of m-oxy-azo-benzol with zinc dust and glacial acetic acid (B. **86,** 4112). Mineral acids transpose it into m-oxy-benzidin. m-Oxy-hydrazo-benzol is the only known free oxy-hydrazo-compound, since o- and p-oxy-azo-benzol, on reduction, decompose at once into aniline and o- or p-amido-phenol respectively. But the alkyl ethers of the oxy-azo-benzols may be reduced to the benzol-o- and p-hydrazo-phenol ethers. Benzol p-hydrazo-phenol ethers undergo, with stannous chloride and HCl, the semidin transposition. Thus, **benzol-p-hydrazo-phenetol** passes into m-ethoxy-o-amido-diphenyl-amine (B. **27,** 2700; **28,** R. 753; **29,** 2680):

$$C_6H_5NHNH[1]C_6H_4[4]OC_2H_5 \longrightarrow \begin{matrix} C_6H_5NH[1] \\ NH_2[2] \end{matrix} \Big\} C_6H_3[5]OC_2H_5.$$

The free hydrazin-phenols are very unstable. o-Hydrazin-anisol $NH_2NH[2]C_6H_4[1]OCH_3$, m.p. 43°, b.p. 240°, see A. **221,** 314.

Sulphonic Acids of Phenol.—The sulphonation of phenol proceeds with the replacement of the o- and p-hydrogen atoms, just as in the nitration process (the sulpho-groups enter the meta-position with reference to one another):

$$C_6H_5OH \begin{cases} \longrightarrow C_6H_4\{[1]OH\ [2]SO_3H \\ \longrightarrow C_6H_4\{[1]OH\ [4]SO_3H \end{cases} \longrightarrow C_6H_3\{[1]OH\ [2]SO_3H\ [4]SO_3H \longrightarrow C_6H_2\{[1]OH\ [2]SO_3H\ [4]SO_3H\ [6]SO_3H$$

o- and **p-Phenol-sulphonic acids** are formed when phenol dissolves in concentrated sulphuric acid; at medium temperatures the former is the more abundant, but readily passes into the *para-* on the application of heat, or even upon boiling with water. This change is due to the fact that o-phenol-sulphonic acid easily sheds its sulpho-group with regeneration of phenol, which then forms p-phenol-sulphonic acid under the influence of sulphuric acid. o-Phenetol-sulphonic acid is

just as easily changed to the p-acid by heating it to 100° (B. **27**, R. 591).

The separation of o- and p-phenol-sulphonic acid succeeds through the crystallisation of its mono-barium salts, the barium ortho-salt $(C_6H_4)OH(SO_3)_2B+H_2O$ crystallising first in coarse needles of the rhombic system. The p-acid is best obtained from the mother-liquor, as in the **magnesium salt** $(C_6H_4)OH(SO_3)_2Mg+8H_2O$, large rhombic columns (B. **40**, 3637). The p-acid is also formed by transposition of phenyl-sulphuric acid.

The free acids can be obtained in crystalline form by the slow evaporation of their aqueous solution. The aqueous solution of the ortho-acid is applied as an antiseptic under the name of **aseptol** (B. **18**, R. 506). The para-acid yields quinone if its sodium salts be oxidised with MnO_2 and sulphuric acid. When the ortho-acid is fused with KOH at 310° it yields pyrocatechin or o-dioxy-benzol; the para-acid does not react at 320°, and at higher temperatures yields diphenols (see Diphenyl).

The action of nitric acid leads easily to the replacement of the sulpho-group by the nitro-group.

With PCl_5 the phenol-sulphonic acids give, in the first place, the phosphor-oxy-chloride derivative of the phenol-sulphonyl chlorides, which, on heating to 180° with PCl_5, are converted into those of the chloro-phenols. On further heating of the latter with PCl_5, we get chloro-benzols:

$$C_6H_4\begin{cases}[1]OH\\[4]SO_3K\end{cases} \longrightarrow C_6H_4\begin{cases}[1]OPOCl_2\\[4]SO_2Cl\end{cases} \longrightarrow C_6H_4\begin{cases}[1]OPOCl_2\\[4]Cl\end{cases} \longrightarrow C_6H_4\begin{cases}[1]Cl\\[4]Cl\end{cases}$$

These reactions may be used to determine the location of the sulphoxyl (B. **6**, 943; A. **358**, 92). If phenyl-sulphonyl chlorides are required for reactions, it is best to acetylate the potassium-phenol sulphonates, then to prepare the acetyl-phenol-sulphonyl chlorides, and finally to remove the acetyl (Anschütz).

From acetyl-phenol-o-sulphonile chloride we obtain, by the action of ammonia, or, better, of diethyl-amine in etheric solution, and with shedding of the acetyl-chloride constituents, **phenylene-sulphonylide** $C_6H_4\left\{\begin{matrix}[1]O—SO_2[2]\\[2]SO_2—O[1]\end{matrix}\right\}C_6H_4$, m.p. 237°, corresponding to salicylide, as suggested by the name.

Iodination of para-sulphonic acid yields **[2, 6]-di-iodo-p-phenol-sulphonic acid** $C_6H_2I_2(OH).SO_3H$, which is used as an antiseptic under the name *sozo-jodol* (B. **21**, R. 250).

Meta-phenol-sulphonic acid [1, 3] is produced when meta-benzol-disulphonic acid is heated to 170°–180° with aqueous potassium hydroxide (B. **9**, 969). The free acid contains two molecules of H_2O. Fusion with potassium hydroxide at 250° converts it into resorcin [1, 3]. When para-benzol-disulphonic acid is heated with caustic alkali, meta-phenol-sulphonic acid is also produced at first, but it yields resorcin later.

Phenol-[2, 4]-disulphonic acid results from the action of an excess of sulphuric acid upon phenol, also upon [1, 2]- and [1, 4]-phenol-sulphonic acid. The solutions of the acid and its salts are coloured a dark red by ferric chloride.

Phenol-[2, 4, 6]-trisulphonic acid is obtained when concentrated sulphuric acid and P_2O_5 act upon phenol. It crystallises in thick prisms with $3\frac{1}{2}H_2O$.

Nitro-phenol-sulphonic acids, see *J. pr. Ch.* 2, **78,** 519.

p-Amido-phenol-sulphonic acid $NH_2[4]C_6H_3(OH)[1]SO_3H[2]$ is formed in small quantity by the action of concentrated H_2SO_4 upon nitro-benzol. There is probably a reduction to β-phenyl-hydroxyl-amine, followed by formation of p-amido-phenol and then amido-phenol-sulphuric acid (C. 1908, II. 587). For other amido-phenol-sulphonic acids, see B. **28,** R. 378, 399; **39,** 3345; C. 1904, I. 1235).

Thio-derivatives of Phenol.

Mercaptans.—Thio-phenol, *phenyl-mercaptan* [*pheno-thiol*] C_6H_5SH, boiling at 168°, with specific gravity 1·078 (14°), is a mobile, ill-smelling liquid. It is made (1) by letting P_2S_5 act upon phenol (*Z. f. Ch.* 1867, 193); (2) by distilling sodium benzol-sulphonate with potassium sulphydrate (B. **17,** 2080); (3) by reduction of benzol-sulpho-chloride, or benzol-sulphinic acid, with zinc and sulphuric acid, or stannous chloride (C. 1900, I. 252; B. **32,** 1147; C. 1904, II. 98); (4) from phenyl-dithio-carbonic ester; (5) from phenyl-magnesium bromide, with sulphur, the compound C_6H_53MgBr being formed first, and then decomposed by acids with rejection of thio-phenol (C. 1908, II. 1349; 1909, II. 193). It manifests great tendency to throw off hydrogen and become phenyl disulphide; hence it often acts as a reducing agent (cp. B. **29,** R. 979). **Mercury thio-phenate** $(C_6H_5S)_2Hg$. **Thio-phenyl-acetal** $C_6H_5.S.CH_2.CH(OC_2H_5)_2$, b.p. 273° (B. **24,** 160). **Thio-phenyl-acetone,** m.p. 34°, and b.p. 266° (B. **24,** 163). Consult B. **24,** 234; **28,** 1120; A. **253,** 161, for mercaptal (Vol. I.) and mercaptal derivatives of thio-phenol. **Phenyl-ortho-thio-formic ester** $C_6H_5S.CO_2.C_2H_5$, m.p. 39° (B. **25,** 347, 252). **Phenyl-dithio-carbonic ester** $C_6H_5S.CSOR$ is formed from diazo-benzol chloride and potassium xanthogenate; it represents a common reaction (C. 1900, I. 252). It yields thio-phenol when saponified. This is the most convenient way of preparing thio-phenols (B. **21,** R. 915), next to the reduction of the sulphinic acids. **Phenyl-thio-carbonic chloride** $C_6H_5S.COCl$, $b.p._{13}$ 104°, and **phenyl-dithio-carbonic chloride** $C_6H_5S.CSCl$, $b.p._{15}$ 135°, are formed by the action of phosgene and thio-phosgene upon sodium thio-phenate. Both compounds, treated with alcohol, phenol, thio-phenol, aniline, etc., have given rise to many thio-phenol derivatives (C. 1907, II. 1159).

Diazo-benzol-thio-phenyl ether $C_6H_5N_2.SC_6H_5$, an oil, is produced from diazo-benzol chloride and phenyl-mercaptan (B. **28,** 3237).

o-Thio-cresol, m.p. 15° and b.p. 188°; the m-body is a liquid, boiling at 195°–202°, while the p-compound melts at 43° and boils at 194°. **Thio-carvacrol** $(CH_3)(C_3H_7)(C_6H_3SH)$, b.p. 235°, see Carvacrol. For further thio-phenols, see B. **32,** 1147; C. 1908, II. 1349.

o-Nitro-thio-phenol $NO_2[2]C_6H_4SH$, m.p. 45°, easily obtained from o-nitro-chloro-benzol with sodium sulphide; it easily oxidises to the disulphide $(NO_2[2]C_6H_4)_2S_2$, m.p. 198°, which is also easily obtained from o_2-dinitro-benzol with sodium sulphide, and from o-nitro-chloro-benzol with alkaline poly-sulphides; p-nitro-chloro-benzol is similarly transformed into **p-nitro-phenyl-disulphide** $(NO_2[4]C_6H_4)_2S_2$. By

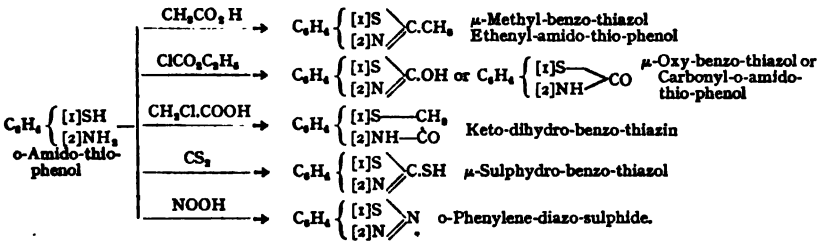
oxidation of these disulphides with HNO_3 we obtain the corresponding nitro-benzol-sulphonic acids (*J. pr. Ch.* 2, **66**, 551).

Of the substitution products of thio-phenol, the o-amido-thio-phenol should be noted on account of its heterocyclic condensation products.

o-Amido-thio-phenol $NH_2[2]C_6H_4[1]SH$ is obtained from ortho-nitro-benzol-sulphonic chloride by reduction with tin and hydrochloric acid. A better method to pursue is to fuse benzenyl-o-amido-thio-phenol with caustic potash (B. **20**, 2259). It melts at 26° and boils at 234°.

m-Amido-thio-phenol (B. **27**, 2816). **p-Amido-thio-phenol,** m.p. 46°, by reduction of aceto-sulphanilic chloride (B. **42**, 3362).

The Condensations of the o-Amido-thio-phenols (compare o-diamines and o-amido-phenols).—(1) *Benzo-thiazols* are formed on heating o-amido-thio-phenol with carboxylic acids, acid chlorides, or acid anhydrides. (2) o-Amido-thio-phenol, by the action of chloro-carbonic esters, forms **μ-oxy-benzo-thiazol** or **carbonyl-amido-thio-phenol.** (3) With chloro- or bromo-acetic acid it yields **keto-dihydro-benzo-thiazin** (*q.v.*). (4) Carbon disulphide produces **μ-sulphydro-benzo-thiazol** (*q.v.*). (5) Nitrous acid converts o-amido-thio-phenol into **o-phenylene-diazo-sulphide** (*q.v.*); at 200°–220° this becomes **diphenylene disulphide**:



See below for the condensation of o-amido-thio-phenol with pyro-catechol to **thio-diphenyl-amine.**

Sulphides.—*Phenyl disulphide* $(C_6H_5)_2S_2$, m.p. 61° and b.p. 310°, results from the oxidation of thio phenol with a chromic acid mixture, or in ammoniacal solution, by the oxygen of the air; by the action of iodine upon aqueous potassium thio-phenate; by heating thio-phenol with benzol-sulphinic acid; by heating thio-phenol or phenyl sulphide with sulphur, etc. Reducing agents decompose it into two molecules of thio-phenol, and alcoholic potash breaks it down into potassium thio-phenate and potassium-benzol sulphinate (B. **41**, 3403).

p_2-Diamido-diphenyl disulphide, *dithio-aniline* $S_2[C_6H_4NH_2]_2$, m.p. 77°, is produced besides thio-aniline on melting up sulphur with aniline and aniline chlorohydrate. On reduction, or on boiling with alcoholic KHO, it is converted into p-amido-thio-phenol (B. **39**, 2427). The diacetyl compound exists in three isomeric forms of m.p. 215°, 182°, and 122° respectively. This isomerism is not as yet explained (B. **41**, 626). Dithio-m-toluylene-diamine, see B. **42**, 743.

Phenyl sulphide $(C_6H_5)_2S$, benzol sulphide, a colourless liquid, with an odour resembling that of leeks, b.p. 292°, has a specific gravity of 1·12. It is formed (1) by distilling phenol with P_2S_5 (along with thio-phenol); (2) from sodium-benzol sulphonate with P_2S_5; (3) by

heating mercury-diphenyl with sulphur (B. **27,** 1171); (4) on heating sulphur with diphenyl sulphone (method of preparation), into which it is also converted by oxidants (B. **26,** 2816); (5) by the action of sulphur hypochloride or finely divided sulphur and Al chloride upon benzene (C. 1905, II. 228). The two last methods are specially suitable for preparing phenyl sulphides. (6) Phenyl sulphide and its homologues are also readily prepared by heating aromatic lead mercaptides with haloid benzols (the bromides are the best adapted for this purpose) (B. **28,** 2322), or sodium mercaptides with iodo-benzols in the presence of powdered copper (B. **39,** 3593).

Diphenylene sulphide or **dibenzo-thio-phene** (*q.v.*) is produced on conducting the vapours of phenyl sulphide through a tube heated to redness.

Fatty aromatic sulphides, which may also be regarded as alcohol ethers of thio-phenols, are produced (1) by the action of iodo-alkylene or dimethyl sulphate upon the sodium salts of the thio-phenols; (2) by heating phenyl-dithio-carbonic ester alone:

$$C_6H_5S.CSOC_2H_5 = C_6H_5SC_2H_5 + COS;$$

(3) by successive action of sulphur and iodo-alkylene upon phenyl-magnesium bromide (C. 1905, I. 80):

$$C_6H_5MgBr \xrightarrow{S} C_6H_5SMgBr \xrightarrow{ICH_3} C_6H_5SCH_3.$$

Phenyl-methyl sulphide $C_6H_5SCH_3$, b.p. 187°–190°; **phenyl-ethyl sulphide** $C_6H_5SC_2H_5$, b.p. 200°–206°. The fatty aromatic sulphides easily add two atoms of bromine or iodine, with formation of dibromides or di-iodides, usually crystallising easily, which, under the action of water, exchange the halogen for oxygen, and form mixed sulph-oxides.

Phenyl-thio-glycolic acid $C_6H_5SCH_2COOH$, m.p. 43·5°, is formed (1) from sodium thio-phenate and monochloracetic acid; (2) by the action of thio-glycolic acid upon diazo-benzol chloride in aqueous solution. In this action the compound $C_6H_5N_2S.CH_2COOH$ is formed first, and passes, on warming, into phenyl-thio-glycolic acid, with rejection of nitrogen (M. **28,** 247; C. 1908, I. 1221).

With dimethyl sulphate the aromatic and fatty aromatic sulphides combine to mixed sulphinic or sulphonium compounds, which change in stability with the number of aromatic radicles. Thus, diphenyl-methyl-sulphonium chloride decomposes on boiling with water, and rapidly on adding alkali, into methyl alcohol and diphenyl sulphide (B. **39,** 3559).

Amido-phenyl Sulphides or Thio-anilines.—*Formation* :—(1) These compounds result when nitro-thio-phenyls are reduced (cp. B. **29,** 2362); (2) from anilines by boiling the latter with sulphur and lead oxide (B. **4,** 384). Sulphur chloride converts the dialkyl-anilines into sym. p-tetra-alkyl-diamido-phenyl sulphides. Silver nitrate and ammonia desulphurise the tetra-alkyl compounds, with the formation of sym. p-tetra-alkyl-diamido-diphenyl oxides—*e.g.* $O[C_6H_4[4].N(CH_3)_2]_2$ (B. **21,** 2056). Upon heating methyl-thio-anilines—*e.g.* thio-p-toluidin —with sulphur to higher temperatures, thiazol derivatives, like *dehydro-thio-toluidin* (see Benzo-thiazol), are produced.

p-Diamido-diphenyl sulphide $S\langle^{C_6H_4.NH_2}_{C_6H_4.NH_2}$, **thio-aniline,** melts at 105°.

o-Diamido-diphenyl sulphide melts at 93° (B. **27,** 2807). See B. **38,** 1130 for isomeric thio-anilines, melting at 80° and 86°.

Thio-p-toluidin $S\begin{matrix}/C_6H_3(CH_3).NH_2\\ \backslash C_6H_3(CH_3).NH_2\end{matrix}$, **diamido-ditolyl sulphide,** melts at 103°. The sodium salts of thio- and dithio-toluidin-sulphonic acids dye unmordanted cotton a greenish yellow (B. **21,** R. 877). They are, therefore, so-called substantive cotton dyes.

The bis-diazo-salts of thio-p-toluidin, which may be produced in the fibre itself, combine with naphthyl-amine-sulphonic acids, and yield diazo-dyes of a brown-red colour (B. **20,** 664).

Thio-diphenyl-imides.—*Thio-diphenyl-amine* $S\begin{Bmatrix}[1]C_6H_4[2]\\ [1]C_6H_4[2]\end{Bmatrix}NH$, is the simplest of these heterocyclic bodies. *Methylene blue,* a most valuable dye, is derived from it. The thio-phenyl-amine group will be discussed later with the hetero six-ring compounds.

Thio-anisol $S(C_6H_4OCH_3)_2$, melting at 46°, and allied bodies, are formed when thionyl chloride or sulphur chloride with aluminium chloride acts upon the phenol ethers (A. **27,** 2540).

Seleno-phenols.—Like sulphur, selenium also attaches itself to phenyl-magnesium bromide, forming $C_6H_5SeMgBr$, from which seleno-phenol is produced with dilute acids.

Seleno-phenol C_6H_5SeH, b.p. 182°, is also formed by reduction of benzol-seleninic acid and diphenyl diselenide, into which it easily passes by oxidation in air. **p-Seleno-cresol,** white flakes, m.p. 47° (C. 1906, II. 1119).

Phenyl selenides and **tellurides** are quite readily obtained from the mercury-diphenyl compounds by the action of selenium and tellurium.

Diphenyl selenide $(C_6H_5)_2Se$ also results upon heating selenium with diphenyl sulphone. Sulphur dioxide escapes at the same time. It boils at 163° (14 mm.). Further action of selenium produces **diphenyl diselenide** $(C_6H_5)_2Se_2$, melting at 63° and boiling at 203° (11 mm.). Reduction changes it to two molecules of *phenyl-selenium hydrate* C_6H_5SeH, melting at 183°. **Diphenyl telluride** $(C_6H_5)_2Te$ boils at 174° (10 mm.); see B. **28,** 1670; **29,** 428. Further aromatic Se and Te compounds, see B. **30,** 2821.

Dihydric Phenols.

Several representatives of this family occur in plants, or have been obtained as decomposition products of plant substances. *Resorcin* or m-dioxy-benzol is especially important from a technical standpoint.

The *general methods of formation* are like those of the corresponding monohydric phenols—(1) by fusing monohalogen phenols, halogen benzol-sulphonic acids, phenol-sulphonic acids, and benzol-disulphonic acids with potassium hydroxide; (2) by diazotising the amido-phenols; and (3) by aromatic dioxy-acids alone or with lime or baryta.

(4) o- and p-Dioxy-benzols also result from the careful reduction of their corresponding quinones. (5) o- and p-Dioxy-benzols are obtained in a straightforward reaction by the oxidation of o- and p-oxy-benzaldehydes and o- and p-oxy-aceto-phenones with H_2O_2 in feeble alkaline solution; m-oxy-benzaldehyde gives no resorcin when treated similarly (C. 1910, I. 634).

Behaviour.—Their behaviour is largely dependent upon the position

of the two hydroxyl groups with reference to one another. The three simplest dioxy-benzols, *pyrocatechol* [1, 2], *resorcin* [1, 3], *hydroquinone* [1, 4], are, therefore, typical representatives of the three groups of dihydric phenols. The behaviour of such bodies can be fully illustrated through them. The dihydric phenols can be changed by chlorine to *hydro-aromatic keto-chlorides*, whose carbon ring may be readily ruptured. Chloroform and caustic potash convert them into dioxy-aldehydes, while they yield dioxy-carboxylic acids with carbon tetrachloride and caustic potash, as well as alkaline carbonate solutions.

Pyrocatechin Group.—All o-dioxy-benzols are coloured green by ferric chloride. They are further distinguished from the m- and p-compounds by their ability to exchange their hydroxyl hydrogen atoms and thus form cyclic esters readily.

Pyrocatechin, pyrocatechol, *o-dioxy-benzol* [1, *2-pheno-diol*] C_6H_4 [1, 2]$(OH)_2$, melting at 104° and boiling at 245°, was first (Reinsch, 1839) obtained in the distillation of catechine (the juice of *Mimosa catechu*), and also from *Moringa tannic acid.*

It is produced in fusing many resins with caustic potash. It occurs in *kino*, the dried juice of different kinds of *Pterocarpus*, *Butea*, and *Eucalyptus*, in beechwood tar, and has been obtained as a by-product in the manufacture of paraffin from bituminous shales at the Messel mine, near Darmstadt, etc. *Pyrocatechol-sulphuric acid* occurs in the urine of the horse and in that of man. It is artificially made (1) by oxidising phenol with hydrogen peroxide or with Caro's acid; (2) by the distillation of pyrocatechuic acid, or [1 CO_2H, 3, 4]-dioxy-benzoic acid; (3) by fusing [1, 2]-chloro-phenol, [1, 2]-bromo-phenol (B. **27,** R. 957), [1, 2]-benzol-disulphonic acid, and [1, 2]-phenol-sulphonic acid with caustic potash; (4) by heating guaiacol-pyrocatechol-monomethyl ether to 200° with hydriodic acid.

On exposure to the air its alkaline solutions assume a green, then brown, and finally a black colour. Lead acetate throws out a white precipitate, $PbC_6H_4O_2$, from its aqueous solution. Neither resorcin nor hydroquinone shows this reaction. Similarly, the formation of antimonyl compounds is characteristic of o-dioxy-benzols, *e.g.* $C_6H_4O_2$. SCOH (C. 1898, II. 598). Pyrocatechin reduces cold silver solutions and alkaline copper solutions. The application of heat is required in the latter case. Silver oxide oxidises it in etheric solution to o-benzoquinone. Pyrocatechin in glacial acetic acid solution is converted by chlorine into tetrachloro-pyrocatechin, tetrachloro-o-quinone, and *hexachloro-o-diketo-R-hexene*; in nitrous acid, to *dioxy-tartaric acid.* Consult p. 214 for the heterocyclic formations obtainable from pyrocatechol. Heated with phthalic anhydride and sulphuric acid, it yields *alizarine* and *hystazarine.* Compare protocatechuic aldehyde and protocatechuic acid. It is used in photography as a developer.

Ethers.—Some ethers of pyrocatechin, such as the mono- and dimethyl ether, as well as the methylene ether, are of special importance, as being closely connected with numerous vegetable substances. such as eugenol, safrol, apiol, vanillin, piperonal, papaverin, etc.

Pyrocatechin-methyl ether, guaiacol, occurs in the creosote from beechwood tar (B. **28,** R. 156). It is produced on heating pyrocatechin with potassium hydroxide and potassium-methyl sulphate to 180°, as well as by heating calcium vanillate, and from veratrol (B. **28,** R. 362).

Ferric chloride gives its alcoholic solution an emerald-green colour (see Vanillin).

p-Nitroso-guaiacol $C_6H_3[2, 1](OCH_3)(OH)[4]NO$, from guaiacol with sodium alcoholate and ethyl nitrite, gives on oxidation *nitro-*, and on reduction *amido-guaiacol* $C_6H_3(OCH_3)(OH)NH_2$ (B. **30,** 2444).

Guaiacol-sulphonic acids, see B. **39,** 3685; C. 1907, II. 1467. Numerous guaiacol derivatives are extensively employed in the treatment of pulmonary tuberculosis.

Dimethyl ether, veratrol $C_6H_4[1, 2](OCH_3)_2$, melting at 15° and boiling at 205°, is prepared by treating the potassium salt of the monomethyl ether with CH_3I, and by distilling vetraric acid with lime.

Pyrocatechin-methylene and **ethylene ether,** b.p. 173° and 216° respectively.

Glyoxal-dipyrocatechin $(C_6H_4O_2)CH.CH(O_2C_6H_4)$, m.p. 89°, from acetylene tetrabromide and sodium pyrocatechin, on hydrolysis, gives **o-oxy-phenoxy-acetic acid** $OHC_6H_4O.CH_2COOH$, m.p. 131°, which also forms direct from monosodium pyrocatechin and chloracetic acid (*J. pr. Ch.* 2, **61,** 345; C. 1900, II. 327), and easily passes into its lactone $C_6H_4\langle{}^{O-CH_2}_{O-CO}$, m.p. 55°, b.p. 243° (B. **40,** 2779).

Ethene-pyrocatechin $C_6H_4\langle{}^{O-CH}_{O-CH}$ and **propene-pyrocatechin** are formed from o-oxy-phenoxy-acetaldehyde and o-oxy-phenoxy-acetone with acetyl chloride or P_2O_5 (C. 1899, II. 620).

Pyrocatechin-diphenyl ether $C_6H_4[1, 2](OC_6H_5)_2$, m.p. 93°, is formed by heating o-dibromo-benzol with potassium phenate in the presence of copper powder. Similarly, we obtain **pyrocatechin-monophenyl ether** $OH[1]C_6H_4[2]OC_6H_5$, m.p. 107°, and **o_2-dioxy-phenyl ether** $[C_6H_4OH]_2O$, m.p. 121°, by melting o-bromanisol with potassium-phenol or guaiacol, from the mono- or dimethyl ether formed at first. Heating with concentrated HBr transforms o_2-dioxy-phenyl ether into **diphenylene dioxide** $C_6H_4\{{}^{[1]O[1]}_{[2]O[2]}\}C_6H_4$, m.p. 119° (B. **39,** 622).

Mono- and dibenzoyl ester, m.p. 130° and 84° (B. **26,** 1076; A. **210,** 261).

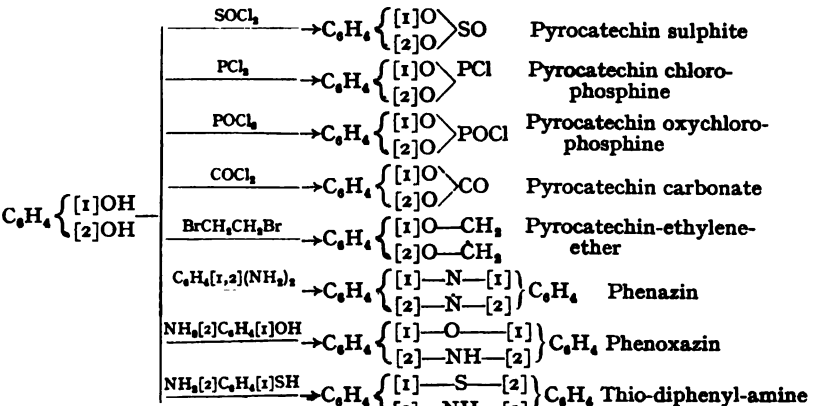
Pyrocatechin sulphite boils at 210°–211° (B. **27,** 2752); **pyrocatechin chloro-phosphine** melts at 130°; **pyrocatechin oxy-chloro-phosphine** melts at 35° (B. **27,** 2569) (see below).

The *carbonic ester* $C_6H_4\{{}^{[1]O}_{[2]O}\rangle CO$ results from the action of chlorocarbonic ester upon pyrocatechin, melts at 118° and boils at 227°. Also from the action of PCl_5 upon pyrocatechin-methylene ether, and decomposition of the resulting dichloro-pyrocatechin-methylene ether $C_6H_4\{{}^{O}_{O}\rangle CCl_2$ with water (C. 1908, I. 1689). This reaction is of importance, inasmuch as by its means the numerous derivatives of pyrocatechin-methylene ether occurring in nature may be transformed into pyrocatechin derivatives otherwise difficult to obtain; cp. Pyrocatechin-aldehyde.

By heating with alcohols or amine bases the pyrocatechin carboxylate is easily broken up into o-oxy-phenol-carbonic esters, or carbaminic o-oxy-phenol esters; with hydrazin hydrate it yields **pyrocatechin-carbonic hydrazide** $HOC_6H_4OCONHNH_2$, which, in alcoholic

solution, reacts easily with aldehydes, but not with ketones (B. **18,** 697; A. **226,** 84; **300,** 135; **317,** 190). **Oxalic ester,** m.p. 185°, from sodium-pyrocatechin and oxal-ethyl-ester chloride (B. **35,** 3452).

HETERO-RING FORMATIONS FROM PYROCATECHOL.—By the replacement of both hydroxyl hydrogen atoms of pyrocatechol, cyclic esters are formed with $SOCl_2$, PCl_3, $POCl_3$, $COCl_2$, and ethylene bromide. o-Phenylene-diamine, o-amido-phenol, and o-amido-thio-phenol condense with pyrocatechin, forming *phenazin, phenoxazin,* and *thio-diphenyl-amine*:



Homologous Pyrocatechols.—Iso-homo-pyrocatechol $CH_3[1]C_6H_3[2,3](OH)_2$, m.p. 47° (B. **24,** 4137). **Homo-pyrocatechol** $CH_3[1]C_6H_3[3,4](OH)_2$, m.p. 51° and b.p. 251°, occurs in the form of its 3-methyl ether as **creosol** $CH_3[1]C_6H_3[3](OCH_3)[4]OH$, b.p. 221°, in beechwood tar, together with phloral (B. **14,** 2005).

Creosol is also formed together with guaiacol (see above) in the distillation of guaiacol resin. Higher homologues of pyrocatechol have been obtained by treating pyrocatechol with aliphatic alcohols and zinc chloride (B. **28,** R. 312).

Ethyl-, propyl- and **iso-propyl-pyrocatechin,** m.p. 39°, 60°, and 78°, are obtained from the corresponding methylene ethers (C. 1904, I. 797; II. 436).

Mono-thio-pyrocatechol $C_6H_4[1,2](SH)(OH)$, m.p. +5° and b.p. 217°, results from the reduction of diphenol disulphide $[C_6H_4OH]_2S_2$, produced on heating sodium phenoxide with sulphur. **o_2-Dioxy-diphenyl sulphide** $[C_6H_4OH]_2S$, m.p. 142°, see B. **39,** 1350.

Diphenylene disulphide, or *thianthrene* $C_6H_4\{[1]S[1]\ [2]S[2]\}C_6H_4$, m.p. 158° and b.p. 360°, should be regarded as a derivative of dithio-pyrocatechol $C_6H_4(SH)_2$. It is made by boiling phenyl sulphide with sulphur, also from benzene, SCl_2, and aluminium chloride, as well as by heating phenylene diazo-sulphide (C. 1899, II. 648; 1905, II. 228). Also by the action of Al_2Cl_3 upon thio-phenol or phenyl disulphide (C. 1909, I. 1652). HNO_3 oxidises it to **thianthrene dioxide** $C_6H_4(SO)_2C_6H_4$, m.p. 230°, which is transposed by heating to 270° into **thianthrene monosulphone** $C_6H_4\langle^{SO_2}_{S}\rangle C_6H_4$, m.p. 279°.

Oxidation converts thianthrene into a disulphone, $C_6H_4(SO_2)_2C_6H_4$. When the latter is heated with selenium, **diphenylene diselenide,** *selenanthrene* $C_6H_4 : (Se_2) : C_6H_4$, m.p. 181° and b.p. 223° (11 mm.), results (B. **29,** 435, 443).

Resorcin Group.

Resorcin, and many of its homologues, combine with phthalic anhydride, the products being the *fluoresceïns* (*q.v.*). The aqueous solutions of the m-dioxy-benzols are coloured *dark violet* by ferric chloride.

Resorcin $C_6H_4[1, 3](OH)_2$, m.p. 118° and b.p. 276°, is produced from *galbanum, asafœtida,* and other resins upon heating them with potash, as well as by distilling the extract of Brazil-wood. It can also be obtained from many m-disubstitution products of benzene, such as [1, 3]-chloro- and iodo-phenol, [1, 3]-phenol-sulphonic acid, [1, 3]-benzol-disulphonic acid, etc., on fusing them with potash or soda at 230°–280°; by the same method from *umbelliferone.*

Even o- and p-compounds (B. **7,** 1175; **8,** 365), especially when fused at high temperatures with caustic alkali, yield resorcin; hence the potash fusion is not available in the determination of position. Resorcin is made on a technical scale from m-benzol-disulphonic acid (*J. pr. Ch.* 2, **20,** 319).

Properties and Behaviour.—Resorcin crystallises in rhombic prisms or plates. It dissolves readily in water, alcohol, and ether, but not in chloroform or carbon disulphide. It possesses a sweet taste. Lead acetate does not precipitate its aqueous solution (distinction from pyrocatechin).

Sodium amalgam reduces resorcin to *dihydro-resorcin* (A. **278,** 20), or *m-diketo-hexamethylene* (B. **27,** 2129). Bromine precipitates it from aqueous solution as tribromo-resorcin, m.p. 111°, while chlorine converts it in glacial acetic acid solution finally into *heptachloro-resorcin* (B. **26,** 498), which can be easily decomposed. Fusion with caustic soda produces phloroglucin, pyrocatechol, and diresorcin $(HO)_2C_6H_3$—$C_6H_3(OH)_2$ (B. **26,** R. 233). The chlorohydrate of a *triresorcin* $C_{18}H_{14}O_4$ (A. **289,** 61) is formed when resorcin is heated with hydrochloric acid.

Ethers and Esters.—The **monomethyl ether** boils at 243° (B. **16,** 151). The **dimethyl ether** boils at 214° (B. **10,** 868). The **diacetyl ester** boils at 278° (B. **16,** 552). The **dicarbonic ester** $C_6H_4(OCO_2C_2H_5)_2$ boils at 300° (B. **13,** 697). The **dibenzoate** melts at 117° (A. **210,** 256). Resorcin combines with the various sugars under the influence of hydrochloric acid (B. **27,** 1356).

Fluoresceïn is produced when resorcin is heated with phthalic anhydride.

If resorcin be heated with sodium nitrite, it forms a deep-blue dye, soluble in water. Acids turn this red (B. **17,** 2617). It is used as an indicator under the name of *lacmoid* (B. **18,** R. 126). Nitric acid, containing nitrous acid, converts resorcin into two dyes—*resorufin* and *resazurin*—derivatives of phenoxazin (*q.v.*) (B. **23,** 718).

When diazo-salts act upon aqueous or alkaline resorcin solutions, azo-dyes and dis-azo-dyes are produced; thus, with diazo-benzol nitrate or chloride the products are: **benzol-azo-resorcin** $(C_6H_5N_2)$ $C_6H_3(OH)_2$, *α*- and *β*-**diazo-benzol-dis-azo-resorcin** $(C_6H_5N_2)_2C_6H_2(OH)_2$

(B. **15,** 2816; **16,** 2858; **17,** 880); while with the diazo-chloride of amido-azo-benzol there results **azo-benzol-azo-resorcin** $C_6H_5N_2.C_6H_4N_2.C_6H_2(OH)_2$ (B. **15,** 2817). The action of amyl nitrite upon an alkaline solution of resorcin produces **4-nitroso-resorcin** $NO[4]C_6H_2[1, 3](OH)_2$ (B. **35,** 4191). On the other hand, **dinitroso-resorcin,** *diquinoyl-dioxime* $C_6H_2[1, 3](OH)_2[4, 6](NO)_2$ or $C_6H_2(O)_2(N.OH)_2[1, 3, 2, 4]$ crystallises in yellow-brown flakes, which detonate on heating to 115° C. (B. **20,** 3133). It occurs in commerce under the names *solid green* or *chlorin* (B. **20,** 3133).

Nitroso-resorcin-monomethyl and -ethyl ether $NO[4]C_6H_3[3]OH[1]OCH_3$ and $-OC_2H_5$ respectively, exist each in two isomeric modifications, one of them being green and unstable, the other yellowish brown and stable. On heating to 130° the former passes into the latter. Both modifications yield the same alkali salt, from solutions of which the yellowish-brown modification is precipitated by acids. This isomerism is perhaps to be interpreted in the sense of the following formulæ: $(RO)C_6H_2(OH)NO$ and $(RO)C_6H_3 : O : (NOH)$, according to which the green form is to be regarded as a true nitroso-phenol, and the yellow as o-quinone-monoxime (*J. pr. Ch.* 2, **70,** 332).

v-Nitro-resorcin $(NO_2)[2]C_6H_3[1, 3](OH)_2$, m.p. 85°, orange needles, volatile with water vapour, is produced by nitrating resorcin-disulphonic acid and splitting of the sulpho-groups with superheated steam (B. **37,** 726).

v-Dinitro-resorcin $(NO_2)[2, 4]C_6H_2[1, 3](OH)_2$, m.p. 148°, by the action of HNO_2 fumes upon resorcin. **Iso-dinitro-resorcin** $(NO_2)_2[4, 6]C_6H_2[1, 3]OH_2$, m.p. 212°.

When cold nitric acid acts on resorcin and various gum resins (galbanum, etc.), or by nitrating meta-nitro-phenol and various dinitro-phenols, we get **trinitro-resorcin** $(NO_2)_3[2, 4, 6]C_6H[1, 3](OH)_2$. It melts at 175°. Ferrous sulphate and lime water colour it green (picric acid colours it blood-red). The **diethyl ester** melts at 120° (C. 1903, II. 829). It is reduced by tin and HCl to **triamino-resorcin ethers.** Stryphinic acid, like picric acid, gives, with hydrocarbons like naphthalin, phenanthrene, etc., and with amines, readily crystallising molecular combinations (C. 1909, I. 526).

Tetranitro-resorcin $(NO_2)_4C_6(OH)_2$, m.p. 152°, on boiling with water, yields trinitro-phloroglucin (C. 1908, I. 724).

Thio-resorcin $C_6H_4[1, 3](SH)_2$, m.p. 27° and b.p. 243°. It results from the reduction of benzol-m-disulphonic chloride, and, when heated with phenyl iso-cyanate, becomes bis-phenyl carbamate, $C_6H_4(SCONHC_6H_5)_2$, m.p. 179° (B. **29,** R. 177; C. 1900, I. 252).

Homologous Resorcins. — **Orcin** is by far the most important body among those which follow:

		M.p.	B.p.	
Orcin	$CH_3[1]C_6H_3[3, 5](OH)_2$	107°	290°	
Cresorcin	$CH_3[1]C_6H_3[2, 4](OH)_2$	104°	269°	(B. **19,** 136)
2, 6-Dioxy-toluol	$CH_3[1]C_6H_3[2, 6](OH)_2$	64°	..	(B. **17,** 1963)
3, 5-Dioxy-o-xylol	$(CH_3)_2[1, 2]C_6H_2[3, 5](OH)_2$	137°	..	(A. **329,** 305)
2, 4-Dioxy-m-xylol	$(CH_3)_2[1, 3]C_6H_2[2, 4](OH)_2$	147°	149°	(B. **23,** 3114)
m-Xylorcin	$(CH_3)_2[1, 3]C_6H_2[4, 6](OH)_2$	125°	277°	(B. **19,** 2318)
***β*-Orcin**	$(CH_3)_2[1, 4]C_6H_2[3, 5](OH)_2$	163°	279°	
Mesorcin	$(CH_3)_3[1, 3, 5]C_6H[2, 4](OH)_2$	149°	275°	(A. **215,** 100)
Di-tertiary-amyl-resorcin	$(C_5H_{11})_2C_6H_2[1, 3](OH_2$	89°	..	(B. **25,** 2653).

Orcin $CH_3[1]C_6H_3[3, 5](OH)_2$,(B. **15,** 2995). It is found in many lichens of the varieties *Roccella* and *Lecanora*, partly free and partly as orsellic acid, or partly as erythrine or diorsellic erythric ester. It is obtained from orsellic acid either by dry distillation or by boiling with lime.

It is obtained by fusing the extract of aloes with caustic potash. It can be prepared synthetically from 3, 5-dinitro-p-toluidin and various other toluol derivatives by the replacement of their side groups by hydroxyl groups (B. **15,** 2990).

Orcin is produced in the distillation of o-dioxy-phenyl acetate of silver $(HO)_2[3, 5]C_6H_3[1]CH_2.CO_2Ag$ (B. **19,** 1451), and upon heating dehydracetic acid (see Vol. I.) with concentrated caustic potash (B. **26,** R. 316). Orcin crystallises in colourless, six-sided prisms containing one molecule of water. It dissolves easily in water, alcohol, and ether, and has a sweet taste. It melts at 56°, when it contains water, but gradually loses this, and melts (dried in the desiccator) at 107°. It boils at 290°. Lead acetate precipitates its aqueous solution; ferric chloride colours it a *blue-violet*. Bleaching lime causes a rapidly disappearing dark-violet coloration. It yields azo-colouring substances with diazo-compounds, and therefore has the 2OH-groups in the meta-position. It does not form a fluoresceïn with phthalic anhydride. Chlorine changes it, when dissolved in glacial acetic acid, into **trichlororcin,** melting at 127°. Dissolved in chloroform it is converted by the same reagent into **pentachlororcin,** or **[1, 3, 5]-diketo-methyl-pentachloro-R-hexene** (B. **26,** 317).

Nitroso-orcin $CH_3.C_6H_2(OH)_2(NO)$ consists of two modifications—dark-red crystals and bright-yellow needles; the first change to the second when heated to 100°–110° (B. **29,** 989).

On allowing its ammoniacal solution to stand exposed to the air, orcin changes to orceïn $C_{28}H_{24}N_2O_7$ (B. **23,** R. 647), which separates out in the form of a reddish-brown amorphous powder. It dissolves in alcohol and alkalies with a dark-red colour, and is reprecipitated by acids. Orceïn forms red lac-dyes with metallic oxides. It is the chief constituent of the colouring matter *archil* (called also *persio, cudbear,* and *purpur*—French), which originates from the same lichens as orcin through the action of ammonia and air. *Litmus* is produced from the lichens *Roccella* and *Lecanora* by the action of ammonia and potassium carbonate. The concentrated blue solution of the potassium salt, when mixed with chalk or gypsum, constitutes the commercial litmus.

Iso-orcin (*cresorcin, γ-orcin*) is obtained by fusing 2, 4-toluol-disulphonic acid with KOH. Also from amido-o-cresol, etc. Also from methylene-bis-resorcin (*q.v.*), resulting from the action of formaldehyde upon resorcin, by reduction with zinc dust and NaOH. By repeating the formaldehyde condensation and by reduction of the resulting methylene bis-cresorcin we obtain **m-xylorcin** (C. 1907, I. 547). Similarly, **3, 5-dioxy-o-xylol** and **1, 2, 6-trimethyl-3, 5-dioxy-benzol** have been obtained from orcin (A. **329,** 305).

p-Xylorcin, or *β-orcin*, from m-dinitro-p-xylol, rapidly acquires a red colour on exposure to air containing ammonia. It has been obtained by distillation from various lichen acids—*e.g. usnic acid. Mesorcin*, or dioxy-mesitylene, is made from dinitro-mesitylene.

Hydroquinone Group.

The p-dioxy-benzenes are usually called hydroquinones, because they are easily obtained by the reduction of the p-quinones, and just as readily reconverted into the latter by ferric chloride.

Hydroquinone, *p-dioxy-benzene* $C_6H_4[1, 4](OH)_2$, melting at 169°, was first obtained by the dry distillation of quinic acid and by digesting its aqueous solution with lead dioxide (Wöhler, A. **65,** 349) :

$$C_6H_7(OH)_4COOH+O = C_6H_4(OH)_2+CO_2+3H_2O.$$

It results also, together with glucose, on boiling the glucoside arbutin with dilute sulphuric acid, and occurs in *Protea mellifera* (B. **29,** R. 416).

It is further formed by the electrolytic oxidation of an alcoholic benzene solution acidulated with sulphuric acid (B. **27,** 1942), and by fusing [1, 4]-iodo-phenol with potassium hydroxide at 180° ; or from [2, 5]-oxy-salicyclic acid, and from para-amido-phenol ; also in small quantities in the distillation of succinates. The most convenient method of preparing it consists in reducing quinone with sulphurous acid :

Extract the hydroquinone from the aqueous solution by shaking with ether, and purify the product by recrystallisation from hot water that has passed through animal charcoal (B. **19,** 1467) and contains sulphur dioxide.

Hydroquinone is dimorphous and crystallises in monoclinic flakes and hexagonal prisms. It decomposes when quickly heated. It dissolves readily in water (in 17 parts at 15°), alcohol, and ether. It forms crystalline compounds with H_2S and SO_2; these are decomposed by water. Ammonia colours the aqueous solution reddish brown. It is only in the presence of ammonia that lead acetate produces a precipitate in the solution of hydroquinone. Oxidising agents (like ferric chloride and chromic acid) convert hydroquinone into quinone ; quinhydrone is an intermediate product.

Hydroquinone, like quinone, forms quinone-dioxime (B. **22,** 1283) with hydroxylamine. It does not combine with diazonium salts to form azo-compounds, but it is oxidised by them to quinone (C. 1908, II. 409).

Hydroquinone is used as a " developer " in photography, and in therapeutics as an antifermentative and antipyretic agent.

Ethers.—**Hydroquinone-monomethyl ether** $CH_3.O[4]C_6H_4[1]OH$ is formed from methyl-arbutin ; and from hydroquinone by heating it with caustic potash, and methyl iodide or potassium-methyl sulphate (B. **14,** 1989). It melts at 53° and boils at 247°. The **dimethyl ether** melts at 56° and boils at 205°. The **ethyl ether** melts at 66° and boils at 246°. The **diethyl ether** melts at 71°. **Diphenyl ether,** m.p. 77° (A. **350,** 97).

Hydroquinone bis-chloro-phosphin $C_6H_4(OPCl_2)_2$ melts at 65° and boils at 200° (65 mm.), while **hydroquinone bis-oxy-chloro-phosphin** $C_6H_4(OPOCl_2)_2$ melts at 123° and boils at 270° (70 mm.) (B. **27,** 2568).

Hydroquinone diacetate $C_6H_4(O.COCH_3)_2$ melts at 123°.

Hydroquinone dibenzoate $C_6H_4(O.COC_6H_5)_2$ melts at 199°.

Homologous hydroquinones are usually prepared by action of sulphur dioxide upon the homologous quinones. **Tolu-hydroquinone** results from the action of hot dilute sulphuric acid upon p-tolyl-hydroxylamine and other p-alkyl phenyl-hydroxylamines, by atomic displacement in the quinols first formed. The intermediate formation of toluquinols is also the cause of the peculiar formation of tolu-hydroquinone during the oxidation of p-cresol with potassium persulphate (B. **41,** 299).

Hydro-p-xylo-quinone bears the name *hydrophlorone*. *Dimethyl-hydro-thymo-quinone*, boiling at 249°, occurs in the ethereal oil of *Arnica montana*, also in " ayapana oil " of *Eupatorium ayapana* (B. **41,** 509; A. **170,** 363). *Ditertiary amyl-hydroquinone* results from hydroquinone and iso-amylene with glacial acetic acid and sulphuric acid (B. **25,** 2650).

		M.p.
Hydro-tolu-quinone (B. **15,** 2981) .	$(CH_3)[1]C_6H_3[2, 5](OH)_2$	124° (A. **215,** 159)
Hydro-o-xylo-quinone . . .	$(CH_3)_2[1, 2]C_6H_2[3, 6](OH)_2$	121° (B. **18,** 2673)
Hydro-m-xylo-quinone . . .	$(CH_3)_2[1, 3]C_6H_2[2, 5])OH)_2$	150° (B. **18,** 1151)
Hydro-p-xylo-quinone . . .	$(CH_3)_2[1, 4]C_6H_2[2, 5](OH)_2$	212° (A **215,** 169)
Hydro-cumo-quinone . . .	$(CH_3)_3[1, 2, 4]C_6H[3, 6](OH)_2$	169° (B. **18,** 1152)
Hydro-thymo-quinone . . .	$(CH_3)(C_3H_7)[1, 4]C_6H_2[2, 5](OH)_2$	139°, b.p. 290°
Ditert. amylhydro-quinone . .	$(C_5H_{11})_2C_6H_2[1, 4](OH)_2$	185°

Substituted Hydroquinones.—Monochloro- and monobromo-hydroquinones have been obtained by the action of concentrated hydrochloric or hydrobromic acid upon p-quinone (B. **12,** 1504). Monochloro-quinone gave dichloro-quinone, etc. (A. **210,** 153). Di-, tri-, and tetrachloro-hydroquinones result from the corresponding chlorinated quinone by the action of SO_2.

Monochloro-quinone	melts at	104° ;	Monobromo-quinone	melts at	110°
[2, 5]-Dichloro-quinone	,,	166° ;	[2, 5]-Dibromo-quinone	,,	186°
[2, 6]-Dichloro-quinone	,,	158° ;	[2, 6]-Dibromo-quinone	,,	163°
Trichloro-quinone	,,	134° ;	Tribromo-quinone	,,	136°
Tetrachloro-quinone	,,	232° ;	Tetrabromo-quinone	,,	244°

Nitro-hydroquinone, m.p. 133°, is formed in the action of ammonium persulphate upon nitro-phenol (*J. pr. Ch.* 2, **48,** 179).

[1, 3]-Dinitro- and **[2, 6]-dinitro-diethyl-hydroquinone,** m.p. 233° and 176° (A. **215,** 149), result from the nitration of hydroquinone diethylate and diacetate. They change into the same **trinitro-diethyl-hydroquinone,** m.p. 130°, and **[2, 5]-dinitro-hydroquinone diacetate,** m.p. 96°. The latter compound exchanges an NO_2 group very readily for $NH.C_6H_5$ (B. **24,** 3824).

Dinitro-hydroquinone results from dinitro-arbutin and dinitro-hydroquinone diacetate. Reduction changes these compounds to amido-hydroquinones (B. **22,** 1656; **23,** 1211). **1, 4-Diamido-hydroquinone** is obtained from the dioxime of 2, 5-dioxy-quinone.

When tetrachloro-quinone is digested with a diluted solution of primary sodium sulphite (A. **114,** 324), we get **dichloro-hydroquinone-disulphonic acid** $C_6Cl_2\begin{cases}(OH)_2\\(SO_3H)_2\end{cases}$. Its aqueous solution is coloured indigo-blue by ferric chloride. When its alkaline solution is boiled it oxidises to potassium *euthio-chronate*.

Monothio-hydroquinone $C_6H_4[1,4](OH)(SH)$, m.p. 30° and b.p. 167° (45 mm.), results from p-diazo-phenol chloride and potassium xanthogenate. **p-Oxy-diphenyl sulphide** $C_6H_5S[1]C_6H_4[4]OH$ results from heating benzol-sulphinic acid with phenol to 150° (C. 1904, I. 130).

Dithio-hydroquinone $C_6H_4[1,4](SH)_2$, m.p. 98°, is obtained from p-benzol-disulphonic chloride or diazo-phenyl disulphide. In the air it gradually oxidises to **p-phenylene disulphide** $[C_6H_4S_2]x$. Methylation converts it into **p-phenylene-dimethyl sulphide** $C_6H_4(SOCH_3)_2$, m.p. 188°, which, on oxidation with HNO_3, yields a **disulphoxide** $C_6H_4(SOCH_3)_2$, m.p. 188°, and a **disulphone** $C_6H_4(SO_2CH_3)_2$, m.p. 260° (B. **42**, 2721).

Trihydric Phenols.

The three isomeric trioxy-benzols are known in the compounds pyrogallol, phloroglucin, and oxy-hydroquinone.

Among the methods of forming polyoxy-benzols we must mention the hydrolysis of polyamido-benzols, which is useful for preparing phloroglucins or sym. trioxy-benzols.

Pyrogallol, *pyrogallic acid* $C_6H_3[1,2,3](OH)_3$, m.p. 132°, is produced by the elimination of CO_2 from gallic acid or pyrogallo-carboxylic acid $CO_2H[1]C_6H_2[3,4,5](OH)_3$, when heated alone, as was first observed by Scheele (1786), or, better, with water to 210°; also by fusing the two p-chloro-phenol-disulphonic acids and hæmatoxylin with potassium hydroxide. It forms white flakes or needles. It dissolves readily in water, with more difficulty in alcohol and ether. Its alkaline solution absorbs oxygen very energetically (B. **14**, 2666), turns brown, and decomposes into carbon dioxide, acetic acid, and brown substances. It is used in gas analysis for the determination of oxygen. Pyrogallol quickly reduces salts of mercury, silver, and gold, with precipitation of the metals, while it is oxidised to acetic and oxalic acids.

Ferrous sulphate containing ferric oxide colours its solution blue, ferric chloride red. Lead acetate precipitates white $C_6H_6O_3.PbO$. An iodine solution imparts a purple-red colour to an aqueous or alcoholic pyrogallol solution. Gallic and tannic acids react similarly. Electrolytic dissociation produces purpuro-gallin (C. 1903, I. 927; 1904, I. 798, 1005).

1-Monomethyl ether, m.p. 40°, b.p.$_{16}$ 147°. **2-Monomethyl ether,** m.p. 87°, b.p.$_{24}$ 155°.

1, 3-Dimethyl ether is found in beechwood creosote. It melts at 51°–52° and boils at 252° (B. **11**, 333; M. **19**, 557). Also by partial saponification of pyrogallol-trimethyl ether. It is notable that the methoxyl, although occupying the middle position, is most easily saponified (C. 1905, II. 1062). Different oxidising agents convert it into *cærulignone*, a diphenyl derivative.

1, 2-Dimethyl ether, b.p. 235° (C. 1904, II. 1118).

The **trimethyl ether** melts at 47° and boils at 235° (B. **21**, 607, 2020).

The **ethyl, diethyl,** and **triethyl ethers** melt at 95°, 79°, and 39°. The syrupy **dimethyl acetate** yields a quinone, $C_6H_2(OCH_3)_2O_2$, with chromic acid; the **triacetate** crystallises.

Pyrogallol carbonate $OHC_6H_2\langle{}^{O}_{O}\rangle CO$, m.p. 133°, from pyrogallol and phosgene in pyridin solution. Hot water regenerates the pyrogallol (B. **37**, 106).

Trichloro-pyrogallol $C_6Cl_3(OH)_3$ melts with decomposition at 177° (B. **20**, 2035).

4-Bromo-pyrogallol $Br[4]C_6H_2[1,2,3](OH)_3$, m.p. 140° with decomposition; **4, 6-dibromo-pyrogallol** $Br_2[4,6]C_6H[1,2,3](OH)_3$, m.p. 158° with decomposition. These are formed by brominating the pyrogallol carboxylate.

Tribromo-pyrogallol $C_6Br_3(OH)_3$, from pyrogallol and bromine, when digested with bromine yields **xanthogallol** $C_{18}H_4Br_{14}O_6$, m.p. 122° (A. **245**, 335).

4-Nitro- and **4, 6-dinitro-pyrogallol**, m.p. 162° and 208°, by nitrogenation of pyrogallol carboxylate. By reduction we obtain the corresponding amido-compounds as easily oxidisable substances, which, on boiling with water or dilute acids, become 1, 2, 3, 4-tetra-oxy- and penta-oxy-benzol respectively (B. **37**, 114).

Methyl-pyrogallol-dimethyl ether $CH_3.C_6H_2(OH)(OCH_3)_2$, m.p. 36° and b.p. 265°, occurs in beechwood creosote (B. **12**, 1371). **1-Methyl-[3, 4, 5]-pyrogallol-[4, 5]-dimethyl ether**, *irodol*, m.p. 57° and b.p. 249°, is formed on distilling iridic acid $CO_2H.CH_2.C_6H_2(OH)(OCH_3)_2$ (B. **26**, 2018).

Propyl-pyrogallol-dimethyl ether, *picamar* $C_3H_7.C_6H_2(OH)(OCH_3)_2$, b.p. 245°, was discovered in beechwood creosote by Reichenbach (B. **11**, 329; A. **8**, 224). **5-Amido-pyrogallol-trimethyl ether** $(CH_3O)C_6H_2NH_2$, m.p. 114°, from trimethyl-gallic amide (A. **340**, 224).

Phloroglucin $C_6H_3[1,3,5](OH)_3$ melts at 219° when it is rapidly heated. Hlasiwetz first obtained it (1855) in the decomposition of *phloretin* (*q.v.*). It can also be prepared from *quercetin*, *hesperidin*, and other *glucosides* (*q.v.*). It is formed from different resins (catechu, kino, gamboge, dragon's blood, and others), on fusion with caustic potash. It is most easily made by fusing resorcin with caustic soda (B. **14**, 954; **18**, 1323); by the fusion of orcin and benzol-trisulphonic acid with sodium hydroxide; also by the saponification and decomposition of synthetically prepared phloroglucin-tricarboxylic ester, which gives up $2CO_2$ (B. **18**, 3454). It is best formed from sym. triamido-benzol, which is not isolated, but hydrolysed by boiling the solution of the double tin-salt obtained direct from trinitro-benzol.

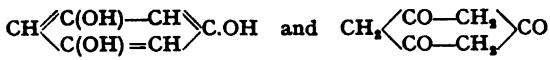
In the same way homologous phloroglucins have been obtained: **mono-**, **di-**, and **trimethyl-phloroglucin** $C_6H_2(CH_3)(OH)_3$, $C_6H(CH_3)_2(OH)_3$, $C_6(CH_3)_3OH_3$, which melt at 215°, 163°, and 184° respectively (C. 1898, II. 537; 1900, I. 600).

It crystallises in large, colourless prisms with $2H_2O$; these effloresce in the air. It loses all its water of crystallisation at 110°, melts at 218°, and sublimes without decomposition. It has a sweetish taste, and dissolves readily in water, alcohol, and ether. Lead acetate precipitates it; ferric chloride colours its solution a *dark violet*.

Chlorine oxidises phloroglucin to *dichloracetic acid* and *tetrachloracetone*. One of the first intermediate products is *hexachloro-triketo-R-hexylene*. For the action of bromine, see B. **23**, 1706. It is con-

verted by reduction into *phloroglucite* or *sym. trioxy-hexamethylene* (B. **27**, 357).

Phloroglucin, in most of its reactions—for example, with phenyl cyanate (see B. **23**, 269),—conducts itself like a trihydric phenol $C_6H_3(OH)_3$; on the other hand, it unites with three molecules of hydroxylamine to form a *trioxime* (see below), hence it may be considered a triketone—[1, 3, 5]-triketo-hexamethylene (B. **19**, 159).



Trioxy-benzol and Triketo-hexamethylene.

In order to explain the trioxime formation it might be assumed that the [1, 3, 5]-trioxy-benzo-formula is the unstable pseudo-form of phloroglucin.

In the keto-form, phloroglucin also reacts in the methylation, with methyl iodide and alkali, which finally leads to **hexamethyl-phloroglucin** or **hexamethyl-triketo-hexamethylene** $C_6(CH_3)_6O_3$, m.p. 80°, b.p. 248°, also formed by methylation of the homologous methyl-phloroglucins, and split up by fuming HCl into di-iso-propyl-ketone and isobutyric acid (B. **23**, R. 462; C. 1899, II. 760). A peculiar phenomenon is the condensation of phloroglucin and its homologues with salicyl aldehyde to *fluorones* (*q.v.*), a reaction in which part of the phloroglucin molecule acts in the keto-form, and another part in the hydroxyl form (M. **21**, 62).

Phloroglucin easily combines with formaldehyde to form *methylene-bis-phloroglucin* $CH_2[C_6H_2(OH)_3]_2$, a diphenyl-methane derivative, which, on reduction with zinc dust and NaHO, decomposes into phloroglucin and methyl-phloroglucin, as well as a little dimethyl- and trimethyl-phloroglucin (A. **329**, 269). This has a close connection with Filix acid from *Aspidium filix-mas*, which, on reduction with zinc dust and NaHO, yields, besides mono-, di-, and trimethyl-phloroglucin, also butyryl-filicinic acid. On prolonged action the latter is split up into n-butyric acid and filicinic acid, probably represented by gem-dimethyl-dioxy-dihydro-keto-benzol (A. **307**, 249; **318**, 230).

Phloroglucin trioxime $C_6H_6(NOH)_3$, a crystalline powder exploding at 155°. Phenyl-hydrazin attaches itself to phloroglucin much as it does to oxalic ester and dioxy-succinic ester.

Trinitroso-phloroglucin $C_6(NO)_3(OH)_3$ (B. **11**, 1375) and **trinitro-phloroglucin** $C_6(NO_2)_3(OH)_3$ yield on reduction **triamido-phloroglucin** $C_6(NH_2)_3(OH)_3$, which, on boiling with MnO_2 and soda, yields *croconic acid* (B. **26**, 2185).

Phloroglucin ethers result from treating phloroglucins with alcohols and HCl, or from methylation with diazo-methane or dimethyl sulphate in etheric solution (C. 1906, II. 1836). **Monomethyl ether,** m.p. 75°–78°, b.p.$_{16}$ 213°, gives a mononitroso-derivative, which may be converted into oxy-methoxy-p-quinone (C. 1903, I. 285), and a dinitroso-derivative, which, on reduction, yields diamido-dioxy-anisol.

Dimethyl ether, m.p. 37°, b.p.$_{17}$ 172°–175°, forms with N_2O_3 an o- as well as a p-nitroso-derivative, 3, 5-*dimethoxy-quinone oxime*, red flakes, and 3, 5-dimethoxy-quinone oxime, yellow needles (M. **21**, 15). **Tri-**

methyl ether, m.p. 52°, b.p. 255°, also obtained by splitting up methyl-dihydro-cotoïn with potash.

Triphenyl ether $C_6H_3(OC_6H_5)_3$, m.p. 112°, by heating sym. tribromo-benzol with K phenate in the presence of Cu bronze (A. **350,** 102). On chlorination products of phloroglucin ether, see C. 1902, II. 739. **Phloroglucin triacetate,** m.p. 105°. **Trithio-phloroglucin** $C_6H_3(SH)_3$, m.p. 58°. **Triacetate,** m.p. 74°. **Trimethyl ether,** m.p. 68° (B. **42,** 3252).

Oxy-hydroquinones result from the reduction of oxy-quinones.

Oxy-hydroquinone $C_6H_3[1, 2, 4](OH)_3$ is produced on fusing hydroquinone with KOH (together with tetra- and hexa-oxy-diphenyl (B. **18,** R. 24). It is crystalline, very soluble in water and ether, and in aqueous solution soon acquires a dark colour. It melts at 140·5°. Ferric chloride colours it a dark greenish brown. Its **triethyl ether** $C_6H_3(O.C_2H_5)_3$ is obtained from trioxy-ethyl-benzoic acid (from æsculetin). It can also be prepared by ethylating ethoxy-hydroquinone. It melts at 34° (B. **20,** 1133). The **trimethyl ether** $C_6H_3(O.CH_3)_3$, from *methoxy-quinone*, boils at 247°. A better method of producing oxy-hydroquinone is from its triacetate, m.p. 97° (A. **311,** 341 ; C. 1899, I. 1094) :

$$C_6H_4O_2+2(CH_3CO)_2O = C_6H_3(OCOCH_3)_3+CH_3COOH.$$

Sodium amalgam reduces it to dihydro-resorcin.

Nitro- and halogen oxy-hydroquinones, see B. **34,** 2837. **Hydroquinone monomercaptan** $C_6H_3(OH)_2SH$, m.p. 120°, is obtained by splitting up **hydroquinone-thio-sulphonic acid** $C_6H_3(OH)_2S.SO_3H$ and analogous sulphuretted hydroquinone derivatives, prepared by the action of sodium thio-sulphate and other thio-acids upon benzo-quinone. Iodine oxidises it to **hydroquinone disulphide** $[C_6H_3(OH)_2]_2S_2$, m.p. 183° (C. 1906, II. 1467).

TETRAHYDRIC PHENOLS.

There are three possible isomerides : (1) **Apionol,** *v-tetraoxy-benzol* [*phenetetrol*] $C_6H_2[1, 2, 3, 4](OH)_4$, needles, m.p. 161°, by boiling amido-pyrogallol chlorohydrate in water. **Dimethyl-apionol** $C_6H_2[1, 2, 3, 4](O.CH_3)_2(OH)_2$, by heating apiolic acid with caustic potash. It melts at 106° and boils at 298°. **Tetramethyl-apionol** $C_6H_2(O.CH_3)_4$ melts at 81°.

[1, 2] - Methylene - 3, 4 - dimethyl - apionol $C_6H_2(O_2 : CH_2)(O.CH_3)_2$, **apione,** is formed when apiolic acid is heated with dilute sulphuric acid. It melts at 69° (B. **24,** 2608 ; **29,** 1806).

1-n-Propyl-2, 3, 4, 5-tetraoxy-benzol is obtained as methylene-dimethyl ether, dihydro-apiol, melting at 25° and boiling at 292°, in the reduction of *isapiol*.

(2) **Unsym. tetraoxy-benzol** $C_6H_2[1, 2, 3, 5](OH)_4$ is an amorphous, glassy mass obtained from iretol by the action of hydrochloric acid at 150°. The **1, 3-dimethyl ether** is prepared by reducing 1, 3-dimethoxy-2, 5-quinone. It melts at 158°. The **tetramethyl ether** melts at 47° and boils at 271° (B. **28,** 2291).

Iretol $CH_3O.C_6H_2(OH)_3$ melting at 186°, is one of its monomethyl ethers. It is formed together with iridic acid on fusing *irigenin* with potash (B. **26,** 2015).

(3) **Sym. tetraoxy-benzol** $C_6H_2[1, 2, 4, 5](OH)_4$ is obtained by reducing 1, 4-dioxy-2, 5-quinone with stannous chloride. It melts at 215°–220°. Its *tetra-acetyl ester* melts at 217° (B. **21,** 3374).

Dichloro-tetraoxy-benzol, hydro-chloranilic acid $C_6Cl_2(OH)_4$ results in the reduction of chloranilic acid with sulphurous acid (A. **146,** 32).

Amido-s-tetraoxy-benzol results from the action of stannous chloride upon nitro-dioxy-quinone, and also **Nitro-amido-s-tetraoxy-benzol** and **diamido-s-tetraoxy-benzol** (B. **18,** 502), by the reduction of nitranilic acid. *Croconic acid* and ammonia are produced on boiling the diamido-body with potash ; oxidising agents convert it into *diamido-dioxy-quinone.*

Hydro-euthiochronic alkali salts, see Euthiochronic acid, below.

Pentahydric Phenols.—Pentaoxy-benzol $C_6(OH)_5H$, colourless crystals, from diamido-pyrogallol on boiling in water (B. **37,** 122). **Penta-acetate,** m.p. 165°. Its diethyl ether, see C. 1903, II. 829.

Hexahydric Phenols.—In describing the benzene ring formations mention was made of the remarkable isolation of *potassium hexaoxy-benzene* or *potassium-carbon monoxide* (discovered by Liebig in 1834), which results upon conducting carbon monoxide over heated potassium (confirmed by Nietzki and Benkiser in 1885). Dilute hydrochloric acid, acting upon the fresh mass, yields hexaoxy-benzene.

Hexaoxy-benzene $C_6(OH)_6$ is obtained from triquinoyl by reduction with stannous chloride and hydrochloric acid. It separates in the form of small, grayish-white needles, which acquire a reddish-violet colour on exposure to the air. They are not fusible, but decompose at about 200°. Concentrated nitric acid oxidises it to triquinoyl.

It forms the **hexacetyl derivative** $C_6(O.C_2H_3O)_6$ when heated with acetic acid and sodium acetate. It is a crystalline mass, melting at 203° (B. **18,** 506).

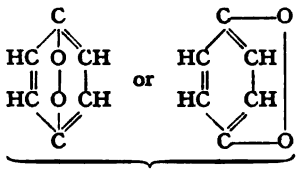
8. Quinones.

This is the designation ascribed to all derivatives of benzene in which 2H-atoms are replaced by 2O-atoms. The replacement is either in the o- or the p-position. We distinguish ortho-quinones and para-quinones. The latter are especially characteristic of the mono-nucleus aromatic hydrocarbons. Metaquinones are not known.

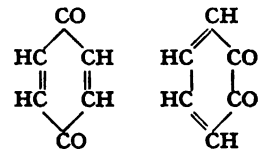
Constitution.—The constitution of the quinones of the aromatic hydrocarbons having one nucleus is not fully established. They are considered either as benzene derivatives, the oxygen atoms being assumed to be linked to one another, or as p-dihydro-benzol derivatives, containing two ketone groups.

The first view compares the quinones to peroxides ; they are indeed powerful oxidising agents. Upon reduction they do not become the p-diglycols of the p-dihydro-benzols, but p-dioxy-benzols, which are true benzene derivatives. The p-quinones yield hydroquinones, and the o-quinones the pyrocatechins. Further, each oxygen atom, by the action of PCl_5, is replaced by *one* chlorine atom. In opposition to the peroxide formula of the para-quinones we have the p-diketone formula, in support of which we can bring forward the formation of a monoxime and a dioxime, as well as the absorption of 2Br and 4Br by para-quinone (*J. pr. Ch.* 2, **42,** 61 ; B. **23,** 3141). Nitroso-phenol is

considered by most chemists to be quinone monoxime. The various formulas for o- and p-quinone are :



Peroxide formula for p- and o-quinone.



Diketone formula for p- and o-quinone.

At the present time the diketone formula is generally preferred.

Ortho-quinones.—The ortho-quinones are much less stable than the para-quinones. The isolation of the simplest o-quinone has only been successfully accomplished quite recently (Willstätter, 1904). Chloro- and bromo-substitution products of o-quinone have been, on the other hand, known for some time (Zincke).

o-Benzo-quinone $C_6H_4[1, 2]O_2$ is formed by gentle oxidation of pyrocatechin with silver oxide in etheric solution (B. **37,** 4744). It exists in two isomeric forms (B. **41,** 2580). When freshly prepared, it forms colourless prisms, which shortly change into the more stable form of bright-red plates, which melt with decomposition at 60°–70°. Chemically, both forms are perfectly equal. They are strong oxidisers, and liberate iodine from acidulated KI solution ; on reduction with sulphurous acid they yield pyrocatechin. The two isomers perhaps correspond to the above peroxide and diketone formulæ. The o-benzol-quinone, in contrast with p-quinone, is odourless and not volatile ; in this respect it more closely resembles the o-quinones of the hydrocarbons with condensed ring systems ; cp. naphtho-quinone and phenanthrene-quinone.

1, 2-Dimethyl-4, 5-benzo-quinone $(CH_3)_2[1, 2]C_6H_2[4, 5]O_2$, long red needles, m.p. 102°, by oxidation of 5-oxy-4-amido-1, 2-dimethyl-benzol with potassium bichromate and sulphuric acid. **Tetrachloro-o-benzo-quinone** $C_6Cl_4[1, 2]O_2$, m.p. 131°, and **tetrabromo-o-benzo-quinone** $C_6Br_4[1, 2]O_2$, m.p. 195°, are formed by the action of chlorine and bromine upon pyrocatechin dissolved in glacial acetic acid (Zincke, B. **20,** 1776). Tetrachloro-benzo-quinone, with aniline, transposes itself into **dianilino-dichloro-o-benzo-quinone** $C_6Cl_2(NHC_6H_5)_2O_2$, which on further action of aniline passes into **dianilino-monochloro-quinone-anile** $C_6HCl(NHC_6H_5)_2(:O)(:NC_6H_5)$, m.p. 180°. This is probably a derivative of p-quinone, since reduction with sulphurous acid changes it to **dianilino-p-quinone-anile** (B. **38,** 4103). The halogen-substituted o-benzo-quinones show a great tendency to form addition products with the most varied classes of bodies. Thus, the tetrabromo-o-benzo-quinone forms with methyl alcohol a very stable combination $(C_6Br_4O_2)_2CH_3OH$, m.p. 261°, which can be acetylated (B. **36,** 454).

Homologous chlorinated ortho-quinones are formed by the action of chlorine upon the corresponding ortho-diamine chlorohydrates. The o-diketo-chlorides first formed may be reduced to chlorinated o-dioxy-benzols, which then give the chlorinated o-quinones by oxidation (B. **27,** 560).

Ortho-benzo-quinone, and several of its homologues, have been

obtained in the form of dioximes by reduction of the corresponding o-dinitroso-benzols; o-nitroso-phenol should be regarded as a monoxime of o-benzo-quinone.

PARA-QUINONES.

Benzo-quinone $C_6H_4O_2$, m.p. 116°, was first obtained in 1838 by Woskresensky upon oxidising *quinic acid*, a hexahydro-tetraoxy-benzoic acid, with manganese peroxide and sulphuric acid. Woskresensky named the new body *quinoyl*, while Berzelius (*Berz. Jahresb.* **19**, 407) proposed the name *quinone*.

Quinone results from the electrolytic oxidation of benzene (C. 1901, I. 348) or from oxidation with silver peroxide (B. **38**, 3964); but most easily from hydroquinone or p-dioxy-benzol by the action of ferric chloride, and from many p-di-derivatives of benzene by oxidation, mostly with potassium bichromate and sulphuric acid; thus, from p-phenylene-diamine, sulphanilic acid, p-amido-azo-benzene, p-amido-phenol, p-phenol-sulphonic acid, p-diamido-diphenyl, or benzidin. It is usually prepared by oxidising aniline with sodium bichromate and sulphuric acid (Nietzki, B. **20**, 2283), in which process a black dye, aniline black, is formed as an intermediate product (B. **42**, 2147). It has also been obtained by oxidising *quinite* (*q.v.*).

Quinone crystallises in golden-yellow prisms. It possesses a peculiar, penetrating odour. It is poisonous and attacks the skin. It distils readily with steam, and dissolves easily in hot water, alcohol, and ether. It turns brown on exposure to sunlight. In the presence of the latter it combines to *dioxy-benzo-phenones* with benzaldehyde, and to dioxy-aceto-phenone with acetaldehyde (B. **31**, 1214).

From acidulated KI solution quinone separates iodine, and this circumstance may be used for the volumetric estimation of quinone solutions (C. 1899, II. 906; B. **43**, 1171).

Reducing agents (SO_2, Zn, and HCl) convert it first into quinhydrone, an addition product of quinone and hydroquinone, which nascent hydrogen changes into hydroquinone.

Hydrogen, in the presence of finely divided nickel, also reduces quinone to hydroquinone at 180°–190°; while at lower temperatures a further set of six H atoms is embodied and 1, 4-cyclohexane-diol is formed (C. 1908, I. 1458).

Concentrated nitric acid dissolves it in the cold, but when the acid is hot it is decomposed, oxalic and prussic acids being formed. Silver peroxide splits it up into maleïc acid and CO_2 (B. **39**, 3715). Bromine converts quinone into quinone di- and tetrabromides, melting at 80° and at 170°–175°. *p-Diketo-hexamethylene*, the hydride corresponding to quinone tetrabromide, has been obtained by starting with succino-succinic ester. With acetic anhydride and concentrated sulphuric acid it combines to form the triacetate of oxy-hydroquinone.

Phosphorus pentachloride converts quinone into p-dichloro-benzene; hydroxylamine chloride changes it to *quinone oxime* or *nitroso-phenol*, and *quinone dioxime*. Phenyl-hydrazin reduces it to hydroquinone; α-alkyl-phenyl-hydrazins show a similar reducing power, changing simultaneously with tetrazones. Nitro- and α-acidyl-phenyl-hydrazins, on the other hand, yield *monohydrazins* of the quinones.

The nuclear H atoms of quinones are relatively easy to replace.

Substitution takes place with or without reduction to hydroquinone. With HCN *dicyano-hydroquinone* is formed, $C_6H_2[1, 4](OH)_2[2, 3](CN)_2$. With benzol-sulphinic acid quinone combines to form *dioxy-diphenyl-sulphone* $C_6H_5SO_2C_6H_3(OH)_2$ (a general reaction of quinoid substances). Thio-acids of the general formula RSH (where R denotes an acid radicle), like thio-sulphuric acid, monothio-carboxylic acids, xanthogenic acids, sulpho-cyanic acid, unite with quinone to sulphuretted derivatives of oxy-hydroquinone: $C_6H_3(OH)_2S.SO_3H$, $C_6H_3(OH)_2S.COC_6H_5$, $C_6H_3(OH)_2S.CS.OC_2H_5$, etc. (C. 1906, II. 1466). With benzo-hydrolene (*q.v.*), water is liberated and compounds like $C_6H_2O_2[CH(C_6H_5)_2]_2$ are formed, belonging to the polynuclear aromatic substances (B. **32,** 2146). With aniline, quinone gives *dianilido-quinone dianile*. With pyridin and quinolin salts, quinone gives addition products (C. 1903, I. 1408). With some metal haloids, it forms addition products of a dark colour (B. **41,** 2568). With halogen hydride, mono- and dihalogen hydroquinone are formed (A. **336,** 108). On boiling with primary alcohols and adding zinc chloride, quinone forms *dialk-oxy-quinone* (B. **34,** 3993).

On the condensation of quinones with aceto-acetic ester to form cumarone derivatives, see the latter. On the addition of diazo-methane to quinone, see B. **32,** 2292.

PHENOL ADDITION PRODUCTS OF QUINONE (A. **215,** 134).

Of the addition products of quinone, those with mono- and dihydric phenols are the most important. In general, quinone unites with two molecules of a monohydric, and with one molecule of a dihydric phenol. But there are exceptions (B. **42,** 1149). These phenol addition products of quinone are distinguished by their intense coloration, and by the ease with which they break up into their components on solution.

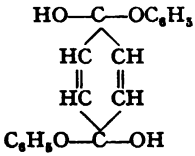
Pheno-quinone $C_6H_4O_2.2C_6H_5OH$, m.p. 71°, by addition of quinone and phenol. It is easily volatilised, crystallises in red needles, and is coloured blue by potash lye, and green by baryta water. Addition products with homologous phenols, see C. 1898, I. 887. On heating the phenols with quinone, with or without H_2SO_4, colourless compounds are formed without evolving water. They differ from pheno-quinone, and must be regarded as probably hydroxylated diphenyl ethers, *e.g.* $OHC_6H_4OC_6H_3(OH)_2$ from resorcin and quinone (B. **30,** 2563; C. 1898, II. 156).

Thio-pheno-quinone $C_6H_4O_2.2C_6H_5SH$ is formed similarly from quinone and thio-phenol. It forms crystals of a dark-bronze colour, colouring blue with NaHO. Gentle oxidation converts it into **3, 6-diphenyl-thio-quinone** $(C_6H_5S)_2[3, 6]C_6H_2[1, 4]O_2$, m.p. 257°, which is easily reduced to 3, 6-diphenyl-hydroquinone. On acetylation of thio-pheno-quinone, hydroquinone diacetate is formed, with splitting of the molecule (A. **336,** 85). Compounds resembling thio-pheno-quinone are also formed from quinone with aliphatic mercaptans.

Quinhydrone $C_6H_4O_2.C_6H_4(OH)_2$.—This is produced by the direct union of quinone with hydroquinone. It appears as an intermediate product in the reduction of quinone or in the oxidation of hydroquinone —*e.g.* in electrolysis (B. **29,** R. 1122),—and is changed by continued oxidation into quinone, and by reduction into hydroquinone. It con-

sists of green prisms or leaflets with metallic lustre, has a quinone-like odour, melts readily, and dissolves in hot water with a brown, in alcohol and ether with a green, colour. When it is boiled with water it decomposes into hydroquinone and quinone. The constitution of these compounds probably corresponds to the following formulas (B. **28,** 1615; **29,** R. 903; A. **336,** 90), in which the two bodies appear either as hemiacetal compounds, or as derivatives of dioxy-p-diketo-hexamethylene:

Pheno-quinone



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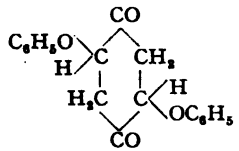
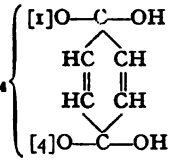
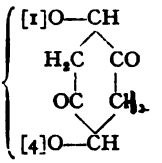


Quinhydrone C_6H_4

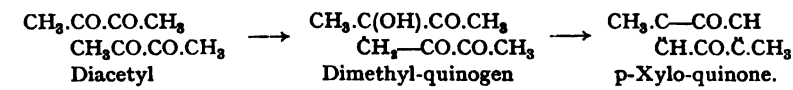


or C_6H_4



Neither formula, however, explains the intense colour or the easy dissociation of these products. There is therefore, of late, a tendency to regard the pheno-quinones and quinhydrones as loose molecular compounds, whose structure cannot be numerically expressed by changes of valency (B. **41,** 1463; *J. pr. Ch.* 2, **79,** 418). On an interpretation of quinhydrones as oxonium compounds, see B. **43,** 3603.

Homologous p-Quinones.—They are produced (1) by the oxidation of the corresponding p-dioxy-benzenes or hydroquinones (even with ferric chloride), of the corresponding p-diamines, p-amido-phenols, such as amido-thymol and many other di-substitution products belonging to the p-series, with ferric chloride, chromic acid, and manganese dioxide and sulphuric acid. (2) Even mono-substituted alkyl-benzenes yield p-quinones, especially when they are oxidised with chromic acid. This is particularly true of amido- and oxy-alkyl-benzenes or alkyl-phenols. Thus, o-toluidin yields **tolu-quinone**, while thymol and carvacrol yield **thymo-quinone** or *thymoïl*. Frequently an alkyl group will be displaced, favouring the p-quinone formation, and be replaced by oxygen —*e.g.* in the oxidation of amido-mesitylene (B. **18,** 1150) to **m-xylo-quinone,** and of pseudo-cumidin to **p-xylo-quinone**. (3) **p-Xylo-quinone** and **duro-quinone** have been synthesised by the action of caustic potash upon the aliphatic α-diketones—*diacetyl-* and *acetyl-propionyl*. In this reaction *quinogens* are first produced; afterwards follow the p-quinones:



Diacetyl — Dimethyl-quinogen — p-Xylo-quinone.

p-Xylo-quinone or *phlorone* occurs in the tar of beechwood.

Properties.—The homologous p-quinones are very similar to their prototype, benzo-quinone. They are also yellow-coloured, possess an odour similar to that of quinone, sublime readily, and behave chemi-

cally like p-benzo-quinone. They form quinhydrones, are easily reduced by sulphurous acid to p-hydroquinones, and combine to nitroso-phenols and quinone dioximes with hydroxylamine :

Toln-quinone	$CH_3[1]C_6H_3[2, 5]O_2$	m.p. 67°
o-Xylo-quinone	$(CH_3)_2[1, 2]C_6H_2[3, 6]O_2$	,, 55°
m-Xylo-quinone	$(CH_3)_2[1, 3]C_6H_2[2, 5]O_2$	,, 102°
p-Xylo-quinone	$(CH_3)_2[1, 4]C_6H_2[2, 5]O_2$	,, 123°
o-Ethyl-benzo-quinone	$(C_2H_5)[2]C_6H_3[1, 4]O_2$	,, 38° (B. **28**, R. 741)
Pseudo-cumo-quinone	$(CH_3)_3[1, 2, 4]C_6H[3, 6]O_2$	,, 11° (B. **27**, 1430)
Duro-quinone	$(CH_3)_4[1, 2, 4, 5]C_6[3, 6]O_2$	,, 111° (B. **29**, 2171 ; **42**, 4161)
Thymo-quinone	$(CH_3)(C_3H_7)[1, 4]C_6H_2[2, 5]O_2$	,, 45°, b.p. 232°.

When an ethereal solution of thymo-quinone is allowed to stand in sunlight for some time, **polythymo-quinone,** m.p. 200°, separates (B. **18,** 3195). See B. **29,** 2176, for **diduro-quinone.**

QUINONE HALOIDS are obtained by the substitution of quinones or by the oxidation of substituted hydroquinones.

A mixture of **tri-** and **tetrachloro-quinone,** called *chloranile,* consists of bright-yellow flakes. It is obtained from many benzene compounds (aniline, phenol, isatin) by the action of chlorine or potassium chlorate and hydrochloric acid (B. **29,** R. 236). It oxidises, and serves as an oxidising agent in the manufacture of colouring matters.

Trichloro- and tetrachloro-quinone are separated from one another by the insolubility of the latter in water. The chloro-quinones are obtained from chloro-hydroquinones by oxidation with nitric acid (A. **146,** 9 ; **210,** 45 ; **234,** 14) :

Monochloro-quinone	m.p. 57° ;	**Monobromo-quinone**	m.p. 55°
[2, 5]-Dichloro-quinone	,, 159° ;	**[2, 5]-Dibromo-quinone**	,, 188°
[2, 6]-Dichloro-quinone	,, 120° ;	**[2, 6]-Dibromo-quinone**	,, 122°
Trichloro-quinone	,, 166° ;	**Tribromo-quinone**	,, 147°
Tetrachloro-quinone		**Tetrabromo-quinone**	

Dibromo-di-iodo-quinone m.p. 225° (B. **38,** 555).

PCl_5 converts tetrachloro-quinone into phosphorus-containing derivatives $C_6Cl_5.OPOCl_2$(?), and then into hexachloro-benzol (B. **24,** 927). It absorbs two atoms of chlorine and becomes **hexachloro-p-diketo-R-hexene,** which caustic soda resolves into dichloro-maleïc acid and trichloro-ethylene. Potassium hydroxide converts trichloro-quinone and tetrachloro-quinone into potassium chloranilate, and tribromo- and tetrabromo-quinone into potassium bromanilate (see B. **32,** 1005).

Amido-quinones.—Amido-quinone is obtained in the form of its aceto-compound $C_6H_3O_2(NHCOCH_3)$, m.p. 142°, by oxidation of 1, 3, 4-diacetamido-phenol, while the 1, 4, 5-diacetamido-phenol yields **2, 5-diamido-quinone** $C_6H_2O_2[2, 5](NH_2)_2$ (B. **30,** 2096 ; **31,** 2399).

Chloranile-amide $C_6Cl_2(NH_2)_2O_2$ is obtained from chloranilic acid. Aniline, acting upon a hot alcoholic solution of quinone, produces not only hydroquinone, but also **dianilido-quinone,** *dianilido-quinone-anile,* and *-dianile,* as well as 2, 5-dioxy-1, 4-quinone (see below).

Quinone-monosulphonic acid $C_6H_3O_2(SO_3H)$, in yellow prisms, is formed by the oxidation of hydroquinone-sulphonic acid and of the two p-amido-phenol-sulphonic acids with PbO_2 in sulphuric acid solution. The **ammonium salt,** golden plates, decomposes at 190°–195° (*J. pr. Ch.* 2, **69,** 334).

Oxy-quinones and Polyquinoyls.

Benzene Oxy-quinones.—Methoxy-quinone $CH_3O[2]C_6H_3 : O_2$, melting at 140°, is produced by oxidising o-amido-anisol $C_6H_4(NH_2).O.CH_3$ with chromic acid.

Chloranilamic acid $C_6Cl_2(NH_2)(OH)O_2$ is obtained from chloranile.

2, 6-Dimethoxy-quinone $(CH_3O)_2[2, 6]C_6H_2O_2$, melting at 249°, results from the oxidation of trimethyl-pyrogallol and trimethyl-phloroglucin (B. **26,** 784).

2, 5-Dioxy-quinone $(HO)_2[2, 5]C_6H_2O_2$ is obtained from dioxyquinone-dicarboxylic acid by boiling with hydrochloric acid, by the oxidation of diamido-resorcin (B. **21,** 2374; **22,** 1285), and by the action of dilute sulphuric acid upon dianilido-quinone (B. **23,** 904; **31,** 2402); and from its ethers by saponification. 2, 5-dimethoxy-, diethoxy-, dipropoxy-quinone, m.p. 166°, 183°, and 187° respectively, generated from quinone by boiling with alcohols and zinc chloride (B. **34,** 3993). Treating with stannous chloride converts the 2, 5-dioxyquinone into sym. tetraoxy-benzol, while aniline converts it into dianilido-quinone. Substitution products of 2, 5-dioxy-quinone have been obtained from tetrachloro- and tetrabromo-quinone as substances. Two of their halogen atoms are exchanged with extreme ease.

Chloranilic acid $C_6Cl_2(OH)_2O_2$, reddish, shining scales, is separated by acids from *potassium chloranilate* $C_6Cl_2(OK)_2O_2+H_2O$, which crystallises in dark-red needles, dissolving with difficulty in water. Potassium chloranilate is produced as well from *tri-* as from *tetrachloro-quinone* by the action of caustic potash. Hypochlorous acid, or chlorine, acting upon chloranilic acid, produces *tri-* or *tetrachloro-tetraketo-hexamethylene*, which change quite readily with the intermediate production of unstable oxy-acids into *trichloro-* and *tetrachloro-triketo-pentamethylene* (B. **25,** 827, 842).

Bromanilic acid $C_6Br_2(OH)_2O_2$ corresponds to chloranilic acid, and with bromine yields similar transposition products to those obtained from it by the action of chlorine.

Nitranilic acid $C_6(NO_2)_2O_2(OH)_2$. It crystallises with water in golden-yellow needles or plates, melts in its water of crystallisation, becomes anhydrous at 100°, and detonates at 170° without melting. It is obtained from hydroquinone and quinone by nitrous acid; on conducting nitrous acid into an etheric quinone solution and cooling, nitranilic quinone is produced, $C_6N_2O_8H_2.C_6H_4O_2$, a combination resembling a quinhydrone, decomposed by dilute potash into quinone and nitranilic acid (B. **33,** 3246). The latter is also generated from chloranile with sodium nitrite, and from terephthalic acid and dioxyquinone-terephthalic acid by means of fuming nitric acid. When nitro-anilic acid is reduced, it yields diamido-tetraoxy-benzene, which renders possible the transition from chloranile to triquinoyl (see below), and potassium hexaoxy-benzene.

Amido-anilic acid, *diamido-dioxy-quinone* $C_6(NH_2)_2(OH_2)O_2$, reddish-blue needles, formed from diamido-tetraoxy-benzene by oxidation in the air or by nitrous acid.

Potassium euthio-chronate $C_6(SO_3K)_2(OH)_2O_2$, see Dichloro-hydroquinone-disulphonic acid.

Tetraoxy-quinone $C_6(O_2)(OH)_4$, formerly called dihydro-carboxylic

acid, is obtained by oxidising the aqueous solution of hexaoxy-benzene by exposure to the air (B. **18,** 507, 1837). It may also be obtained from diamido-dioxy-quinone by boiling with hydrochloric acid, as well as by the action of concentrated nitric acid upon inosite. Metallic black needles, with a green, metallic reflex. It is a strong dibasic acid.

Nitro-dioxy-quinone-sulphonic acid $C_6NO_2(OH)_2O_2(SO_3H)$. Its tri-potassium salt, yellow needles, is produced by the action of K nitrite upon K-dichloro-hydroquinone disulphonate (B. **38,** 453).

Tetrathio-ethyl-quinone $C_6O_2(SC_2H_5)_4$, colourless prisms, m.p. 59°, from chloranil and sodium mercaptan (C. 1905, II. 1427).

Homologous oxy-quinones result upon treating haloid quinone homologues with caustic potash, and on heating amido- or anilido-quinones with alcoholic hydrochloric acid or sulphuric acid. **Dianilido-tolu-quinone,** melting at 232°, yields anilido-oxy-tolu-quinone, decomposing at 250°, and dioxy-tolu-quinone $CH_3.C_6H(OH)_2O_2$, melting at 177° (B. **16,** 1559). **Dioxy-m-xylo-quinone** $C_6(CH_3)_2O_2(OH)_2$, red flakes, m.p. 167°, from amido-dimethyl-phloro-glucin (M. **21,** 1). **Oxy-thymo-quinone** $(C_3H_7)(CH_3)C_6H(OH) : O_2$, melting at 166°, is obtained from brom- or methyl-amido-thymo-quinone. **Dioxy-thymo-quinone** melts at 213° (B. **14,** 95).

p-Dialkylated dioxy-quinones, like **p_2-dimethyl-dioxy-benzo-quinone** $C_6(CH_3)_2[3, 6](OH)_2[2, 5]O_2[1, 4]$, are formed as by-products during the production of homologous oxal-acetic esters by condensation of oxalic ester with fatty acid esters by means of sodium in etheric solution. They form red or yellowish-red compounds, dissolving in alkalies with a violet colour. By reduction they give homologous tetraoxy-benzols. On boiling with excess of soda lye, they are split up into formations of homologous succinic acids. **p_2-Dimethyl, diethyl-,** and **di-iso-propyl-dioxy-benzo-quinone** melt at 245°, 218°, and 154° respectively (A. **361,** 363).

It is also very probable that **pipitzahoic acid** $C_{15}H_{19}(OH) : O_2$, found in the root of *Trixis pipitzahuac,* and melting at 103°, belongs to the oxy-quinones, containing but one nucleus. It recalls, by its behaviour, oxy-thymo-quinone. **Oxy-pipitzahoic acid** $C_9H_{18} : C_6(OH)_2 : O_2$ (?), melts at 138° (A. **237,** 90).

Polyquinoyl Compounds.—As mentioned under benzo-quinone (p. 226), Woskresensky originally called this compound *quinoyl.* Nietzki and Benckiser introduced this name in a different sense. They applied it to the quinone group O_2, when they discovered dioxy-diquinoyl-benzene and triquinoyl-benzene to be bodies containing more than one quinone group O_2. For simplicity's sake they abridged these names to *dioxy-diquinoyl* and *triquinoyl.*

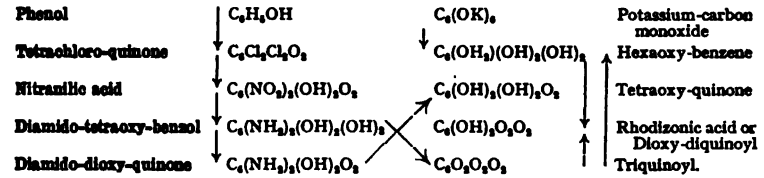
Dioxy-diquinoyl $C_6(O_2)(O_2)(OH)_2$, called *rhodizonic* acid, is prepared by reducing triquinoyl with aqueous sulphurous acid (B. **18,** 513). It consists of colourless leaflets, very readily soluble in water. It decomposes quite rapidly in aqueous solution. The *potassium salt* $C_6O_4(OK)_2$ may be obtained by treating the acid with potashes, and also by washing potassium-hexaoxy-benzene (potassium-carbon monoxide) with alcohol. It forms dark-blue needles, dissolving in water with an intense yellow colour (B. **18,** 1838).

Consult B. **28,** 3140 for the constitution of rhodizonic acid.

Triquinoyl $C_6O_6+8H_2O$ is probably hexaketo-hexamethylene (B. **20,**

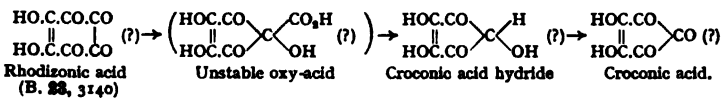
322). It results upon oxidising dioxy-diquinoyl and diamido-tetraoxy-benzene with nitric acid. It is a white, micro-crystalline powder (B. **18**, 504; A. **850**, 330). It melts about 95°, giving up water and CO_2. It is likewise decomposed by warming it with water to 90°. Stannous chloride reduces it to hexaoxy-benzene, which is oxidised in alkaline solution to tetraoxy-quinone $C_6(O_2)(OH)_4$ (see above).

Nietzki and Benckiser (1885) discovered the relations existing between potassium-carbon monoxide and phenol. Compare the following:



Addendum.—Pentacarbocyclic compounds are readily formed from triquinoyl and dioxy-diquinoyl, as well as from some hexa-substitution derivatives of benzene, from which these polyquinoyl bodies arise—*e.g.* hexaoxy-benzene, diamido-tetraoxy-benzene, etc. They will accordingly be discussed after the polyquinoyls.

Croconic acid hydride $C_5H_4O_5$ is formed upon treating rhodizonic acid with excessive alkali, or croconic acid with hydriodic acid. It is distinguished by its *barium salt* $C_5H_2BaO_5+2H_2O$. Its formation is probably due to the breaking down of an unstable oxy-acid, produced by the action of the caustic alkali upon two of the combined CO-groups of the rhodizonic acid (see the rearrangement of benzilic acid):



Rhodizonic acid (B. **22**, 3140) — Unstable oxy-acid — Croconic acid hydride — Croconic acid.

Croconic acid $C_5O_3(OH)_2+3H_2O$ consists of sulphur-yellow leaflets; it loses its water of crystallisation at 100°. It dissolves very readily in water and alcohol, and is produced by the alkaline oxidation of most of the hexa-substituted benzene derivatives—*e.g.* hexaoxy-benzene, dioxy-diquinoyl, diamido-tetraoxy-benzene, etc. The hydride of croconic acid is an intermediate product, which changes quite readily to the acid. Triquinoyl, when boiled with water, decomposes into carbon dioxide and croconic acid:

$$C_6O_6+H_2O = C_5H_2O_5+CO_2.$$

Its *potassium salt* $C_5O_5K_2+3H_2O$ crystallises in orange-yellow needles; hence the name, from κρόκος, safran (Gmelin, 1825). When oxidised with nitric acid or chlorine the product is:

Leuconic acid $C_5O_5+4H_2O$, *pentaketo-cyclo-pentane*, which is reconverted into croconic acid by sulphur dioxide. This acid bears the same relation to croconic acid that rhodizonic acid bears to triquinoyl. It is very soluble in water, but dissolves with difficulty in alcohol and ether. It crystallises in small colourless needles. The **penta-oxime** $C_5(:N.OH)_5$, decomposing at 172°, is isomeric with fulminic acid,

cyanic acid, cyanuric acid, and by reduction yields **penta-amido-pentol** $C_5H(NH_2)_5$, *penta-amido-cyclo-pentadiene* (B. **22**, 916).

Quinone-nitrogen Derivatives.

The quinone oxygen atoms can be replaced by N(OH), NCl, NH, NC_6H_5, and similar groups.

Quinone Dioximes.—In connection with the p-nitroso-phenols, and in the explanation of Fittig's diketone formula for p-quinone, it was indicated that many chemists regarded the p-nitroso-phenols, resulting from the action of hydroxylamine hydrochloride upon the p-quinones, as *monoximes* of the latter. Indeed, the p-nitroso-phenols, by action of hydroxylamine hydrochloride, change to *p-quinone dioximes*. It is true these two classes can be viewed as constituted according to the peroxide formula of the p-quinones. o-Quinone dioximes are formed by the reduction of o-dinitroso-benzols; by splitting off water they easily pass into anhydrides, the so-called *furazane* derivatives (A. **307**, 28).

Their dioximes unite with acetic anhydride to diacetyl compounds. *p-Dinitroso-benzols* are produced by the oxidation of their alkaline solutions (also on exposure to the air). Nitric acid oxidises them to *p-dinitro-benzols* (B. **21**, 428).

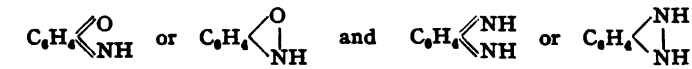
p-Quinone dioxime $C_6H_4(N.OH)_2$ consists of colourless or yellow needles, which decompose at 240°.

Tolu-quinone dioxime deflagrates at 220° (B. **21**, 679). **p-Xylo-quinone dioxime** melts at about 272° (B. **20**, 978). **Mono-** and **dibenzoyl-quinone dioxime,** see C. 1903, I. 1409.

o-Quinone dioxime $C_6H_4[1, 2](NOH)_2$, small yellow needles, dissolves in alkalies with a blood-red colour, and passes into its colourless anhydride $C_6H_4N_2O$ on simply standing, or warming in alkaline solution (B. **40**, 4344).

Dinitro-resorcin and hydroxylamine yield **diquinoyl trioxime** $C_6H_2O(NOH)_3$, and **diquinoyl tetroxime** $C_6H_2(NOH)_4$. The latter, oxidised with sodium hypochlorite, yields tetranitroso-benzol (B. **30**, 181; **32**, 508).

Quinone imines are to be regarded as diketones, or as peroxides in which the oxygen is represented by the imino-group (: NH) or the alkyl-imino-group (: NR), corresponding to the formulæ



Quinone-mono-imine Quinone di-imine.

They are formed from p-amido-phenol or p-phenylene-diamine, by gentle oxidation with silver oxide and lead peroxide in etheric solution. In contrast with the quinones, they are colourless and exceedingly unstable. They are strong oxidisers, smell like quinones, and are volatile. On warming with mineral acids they decompose into ammonia and quinone. By reduction with sulphurous acid or stannous chloride and HCl, they are reconverted into the original substances, p-amido-phenol and p-phenylene-diamine. Owing to the easy decomposition of the o-quinones, the isolation of the o-quinone imines, which are probably even more unstable, has not been accomplished. The o-quinone

di-imine, probably first formed by the oxidation of o-phenylene-diamine, polymerises at once to o-azo-aniline.

$$2C_6H_4\begin{cases}[1]:NH\\[2]:NH\end{cases}\longrightarrow C_6H_4\begin{cases}[1]N{=}{=}N[1]\\[2]NH_2H_2N[2]\end{cases}C_6H_4$$

(B. **38,** 2348).

Quinone mono-imine O[1]C_6H_4[4]NH, colourless prismatic crystals, which quickly turn dark in solution, and decompose in a short time when dry (B. **37,** 4607).

Quinone monomethyl-imine O[1]C_6H_4[4]NCH_3, formed by oxidation of p-methyl-amido-phenol $OHC_6H_4NHCH_3$ with Ag_2O or PbO_2. It is still more unstable than the unmethylated imine, and deflagrates immediately on formation (B. **38,** 2251).

Quinone di-imine NH[1]C_6H_4[4]NH, m.p. about 129°, is also formed by reduction of p-quinone dichlor-imine with HCl in etheric solution. It forms colourless monoclinic prisms, which are quickly browned in air (B. **37,** 4606). With sodium disulphite it unites to form a mixture of p-amido-phenol-sulphonic acid and p-phenylene-diamine-sulphonic acid.

Quinone monomethyl-di-imine NH[1]C_6H_4[4]NCH_3, m.p. 64°–67°, and **quinone dimethyl-di-imine** CH_3N[1]C_6H_4[4]NCH_3, m.p. 93°, result, like the simple quinone di-imines, from the oxidation of monomethyl- or sym. dimethyl-p-phenylene-diamine. They form almost colourless crystals, dissolving with a light-yellow coloration. They are as unstable as the non-methylated quinone di-imine (B. **38,** 2249; **40,** 2672).

Unsym. quinone-dimethyl-di-imonium nitrate $NH:[1]C_6H_4[4]:N(CH_3)_2NO_3$, HNO_3 is obtained in the form of very unstable light-yellow prisms by the oxidation of unsym. dimethyl-p-phenylene-diamine with nitrous gases. It decomposes rapidly, and deflagrates on heating. With one molecule of its hydro-compound the unsymmetrical dimethyl-p-phenylene-diamine, it unites to form a body, $[NO_3NH_2:C_6H_4:N(CH_3)_2NO_3+NH_2C_6H_4N(CH_3)_2]$, of a structure resembling quinhydrone, green crystals dissolving in water with a red fuchsine coloration. These interesting compounds, called *Wurster's red* after their discoverer, result from the partial oxidation of salts of unsym. dimethyl-p-phenylene-diamine (B. **12,** 1803, 2071). The corresponding **bromo-hydrate,** m.p. 147° with decomposition, in green crystals, results from the action of one atom bromine upon unsym. dimethyl-p-phenylene-diamine in glacial acetic acid solution. Reducers bleach the deep-red solution, with formation of phenylene-diamine. Oxidisers do the same, and form the entirely quinoid compound (B. **41,** 1458).

Analogous blue compounds are obtained by starting from tetramethyl-p-phenylene-diamine (*Wurster's blue*, B. **12,** 1807; **41,** 1473). Unstable oxidation products coloured an intense green, or blue, have also been obtained from p-phenylene-diamine and dibromo-p-phenylene-diamine (C. 1904, I. 1073; B. **38,** 3354).

Amido-quinone imine NH_2[2]C_6H_3[1]O[4]NH and its homologues are formed by oxidation of 2, 4-diamido-phenols with ferric chloride. The bichromate forms greenish-black, brilliant grains, dissolving in water with a red colour (B. **39,** 3437).

Diamido-quinone imine $(NH_2)_2C_6H_2(O)(NH)$(?) is obtained from triamido-phenol (A. **215**, 351).

Quinone Chlorimines.—They are produced from p-amido-phenols and p-phenylene-diamines (their HCl salts) by oxidation with an aqueous solution of bleaching lime. They revert to p-amido-phenols or p-phenylene-diamines upon reduction. The monochlorimines form the indo-phenol dyestuffs with phenols and tertiary anilines.

Quinone monochlorimine O[1]C_6H_4[4]NCl forms golden-yellow crystals, which melt at 85°, volatilise readily with steam, and smell like quinone. It is easily soluble in hot water, alcohol, and ether. When boiled with water it decomposes into NH_4Cl and quinone (*J. pr. Ch.* 2, **23**, 435).

Quinone dichlorimine C_6H_4[1, 4](N_2Cl_2) crystallises in needles which deflagrate at 124° (B. **12**, 47).

Trichloro-quinone chlorimine, m.p. 118° (*J. pr. Ch.* 2, **24**, 429).

Dibromo-quinone chlorimine, m.p. 80° (B. **16**, 2845).

Quinone-phenyl-hydrazones.—While phenyl-hydrazin and alkylated phenyl-hydrazins are oxidised by quinone, o-nitro- and o, p-dinitro-phenyl-hydrazins give condensation products which may be interpreted as p-oxy-azo-compounds, being identical with the coupling products of diazotised o-nitro- or o, p-dinitraniline and phenol (A. **357**, 171). With α-acetyl- and benzoyl-phenyl-hydrazins, on the other hand, true quinone-phenyl-hydrazones are generated.

Quinone-acetyl- and **benzoyl-phenyl-hydrazone** $O : C_6H_4 : NN(Ac)C_6H_5$, m.p. 118° and 171° respectively, which, however, are easily transposed into the acylated p-oxy-azo-compounds $AcOC_6H_4N_2C_6H_5$ (B. **40**, 1432). This reaction has acquired a special importance for determining the constitution of the oxy-azo-compounds. The **o-quinone-benzoyl-phenyl-hydrazone** (?) yields, by its hydrolytic decomposition, o-oxy-azo-benzol (C. 1909, I. 1093).

Quinone-oxime-hydrazones result from the action of benzoyl-hydrazin and benzoyl-phenyl-hydrazin upon nitroso-phenols. **Quinone-oxime-benzoyl-hydrazone** $(HON) : C_6H_4 : NNH.COC_6H_5$, m.p. 210° with decomposition. **Quinone-oxime-benzoyl-phenyl-hydrazone** $(HON) : C_6H_4 : NN(COC_6H_5)C_6H_5$, on boiling with HNO_3, yields p-nitro-azo-benzol (A. **348**, 176).

Quinone semi-carbazone and **Amido-guanidone.**—The quinones react more readily with semi-carbazide and with amido-guanidin than with phenyl-hydrazin. **Quinone mono-** and **bi-semi-carbazone** $C_6H_4O(NNHCONH_2)$ and $C_6H_4(NNHCONH_2)_2$, m.p. 171° and 243° respectively, are obtained from quinone and HCl semi-carbazide. **Quinone mono-** and **bis-amido-guanidone** $C_6H_4O[NNHC(NH)NH_2]$ and $C_6H_4[NNHC(NH)NH_2]_2$ are obtained from amido-guanidin nitrate and quinone in the presence of nitric acid (A. **302**, 311). The quinone mono-semi-carbazone and mono-amido-guanidone are probably oxy-azo-compounds (A. **334**, 143).

Quinone Azines. — *p-Quinone azine* O[4]C_6H_4[1]N.N[1]C_6H_4[4]O deflagrates at 158°. It is formed by oxidation of p-azo-phenol with Ag_2O and PbO_2 in etheric solution. It is obtained in the form of dark orange prisms or dark yellow rhombohedral flakes. It is stable in air, and is odourless and not volatile. Reduction with sulphurous acid or phenyl-hydrazin reconverts it into p-azo-phenol,

while stannous chloride and HCl produce p-amido-phenol. With one molecule of p-azo-phenol it combines to form a compound resembling quinhydrone, blue-black needles of m.p. 182°, also obtainable by direct oxidation of p-azo-phenol. o- and m-Azo-phenol yield no quinone azines.

Quinone Diazides.—It has been already pointed out in connection with the diazo-salts of the o- and p-amido-phenols that the corresponding diazo-hydrates easily pass into yellow anhydrides related to the quinones, and probably interpretable as **o- and p-quinone diazides** $\begin{matrix}N\\N\end{matrix}\!\!>\!C_6H_4:O$. Similar behaviour is shown by the diazonium salts of **p-amido-diphenyl-amine** $NH_2C_6H_4NHC_6H_5$, which, on treatment with ammonia, form **p-quinone diazide anile** $\begin{matrix}N\\\|\\N\end{matrix}\!\!>\!C_6H_4:NC_6H_5$ (B. **35**, 888).

Quinone-phenyl mono-imine, *quinone monoanil* $C_6H_4\langle\begin{matrix}O\\|\\NC_6H_5\end{matrix}$ or $C_6H_4\langle\begin{matrix}O\\\|\\N.C_6H_5\end{matrix}$, m.p. 97°, consists of fiery-red crystals. It is formed upon oxidising p-oxy-diphenyl-amine in benzene solution with mercuric oxide, and upon reduction reverts to the same (B. **21**, R. 434).

Indo-phenols and **Indo-anilines.**—These compounds are obtained from quinone monoanile or quinone phenyl-imide by replacing the p-hydrogen atom of the anile group by an OH or an NH_2 group. They are dyes. Like many members of this class, they are decolorised by the addition of hydrogen. The resulting bodies are leuco-compounds, p-di-substituted diphenyl-amines. (Nomenclature, **B. 29**, R. 94.)

Indo-phenols are produced (1) by allowing the quinone chlorimines to act upon phenols; (2) by oxidising a mixture of a p-amido-phenol and phenol. They dissolve in alcohol with a red colour, and possess a character similar to phenol. Their salts, with the alkalies and ammonia, dissolve in water with a *blue* colour.

Quinone phenol-imine $C_6H_4\langle\begin{matrix}N.C_6H_4OH\\|\\O\end{matrix}$ also results upon heating *phenol blue* with soda lye (B. **18**, 2916), but, owing to its instability, cannot be obtained in a free condition. By reduction it changes to colourless p-dioxy-diphenyl-amine from which it can be recovered by HgO (B. **32**, 689). **Dibromo-quinone phenol-imine** $C_6H_2Br_2\langle\begin{matrix}N.C_6H_4OH\\|\\O\end{matrix}$, from dibromo-quinone chlorimine, is more stable than quinone-phenol-imine. Free dibromo-phenol-imine crystallises in dark-red prisms having a metallic lustre; they dissolve in alcohol and ether with a fuchsine-red colour. Strong mineral acids decompose it into dibromo-phenol and quinone.

The **Indo-anilines** are produced (1) by the action of quinone chlorimine upon dimethyl-aniline in alcoholic solution; (2) by the action of nitroso- and nitro-dimethyl-aniline upon phenol in alkaline solution, especially in the presence of reducing agents (Witt, 1879); (3) by the oxidation in *alkaline* solution (with sodium hypochlorite) of a mixture of a p-phenylene-diamine with a phenol, or of a p-amido-phenol with a primary monamine, or by means of lead peroxide or manganese

peroxide in the presence of di-sodium phosphate (1877, Nietzki ; B. **28,** R. 470 ; C. 1908, I. 437 ; 1906, II. 477).

The indo-anilines are feeble bases. They are rather stable towards the alkalies ; acids quickly decompose them into quinones and the p-phenylene-diamines. They are changed to the leuco-compounds ; amido-oxy-diphenyl-amines, by reduction (absorption of two hydrogen atoms) ; these dissolve readily in alkalies, and are readily reconverted (oxidised) into indo-anilines (by exposure of their alkaline solution to the air). The free indo-anilines have a deep-blue colour, and can be applied as dyestuffs. For this purpose they are converted into their alkaline leuco-derivatives, which are soluble, and the material is impregnated or printed with these. Oxidation (by exposure to the air or with $K_2Cr_2O_7$) develops the colour. The simplest aniline is **quinone anilin-imine** $C_6H_4\langle{}^{N.C_6H_4.NH_2}_{O}$, a violet dye, formed by the oxidation of p-phenylene-diamine $C_6H_4(NH_2)_2$ with phenol. **Quinone dimethyl-anilin-imine** (phenol blue) $C_6H_4\langle{}^{N.C_6H_4:N(CH_3)_2}_{O}$ results from unsym. dimethyl-p-phenylene-diamine and phenol. It has a greenish-blue colour and dissolves in acids with a blue colour. When boiled with soda lye it splits off dimethyl-amine and becomes quinone-phenolimine. Sulphuric acid decomposes it into quinone and dimethyl-p-phenylene-diamine. This is a general reaction, hence can be used opportunely for the preparation of quinones (B. **28,** R. 471 ; **29,** R. 24).

QUINONE PHENYL-DI-IMINES.

Quinone monophenyl-di-imine $C_6H_5N : C_6H_4 : NH$, light-yellow prisms, m.p. 89°, by oxidation of p-amido-diphenyl-amine with silver oxide or lead peroxide in etheric solution. It is also formed, besides quinone monoanile, during the gentle oxidation of aniline in an aqueous alkaline solution. Water splits it up, even when cold, into ammonia and quinone monoanile. On heating with dilute sulphuric acid it passes into quinone. Mineral acids readily polymerise it to form a green dye, *emeraldin*. The latter is also formed when p-amido-diphenyl-amine is oxidised in an acid solution with ferric chloride or hydrogen peroxide, also by reduction of nitro-benzol in a hydrofluosilicic acid solution, the body first formed being p-amido-diphenyl-amine. The free base separated from emeraldin, the so-called *azurin*, m.p. 165°, forms deep-blue prisms, and probably has the constitution $C_6H_5NH.C_6H_4NH.C_6H_4N : C_6H_4 : NH$. By oxidation with lead peroxide in benzene solution this half-quinoid azurin or emeraldin, respectively, may pass into a doubly quinoid *red* imine $C_6H_4N : C_6H_4N : C_6H_4N : C_6H_4 : NH$, which, after the manner of quinone monophenyl-di-imine, polymerises, under various conditions, to a black dye called aniline black (B. **40,** 2665 ; **42,** 4123).

Aniline black* is one of the oldest known organic dyestuffs, and is distinguished by its permanence. It is formed by the oxidation of aniline salts with potassium bichromate and sulphuric acid, ammonium

* E. Noelting and R. Lehne, *Anilinschwarz und seine Anwendung in Färberei und Zeugdruck*, 2nd ed., Berlin, 1904, Springer.

persulphate, or potassium chlorate, in the presence of oxygen carriers such as copper sulphate, potassium ferrocyanide, ammonium vanadate, etc. In its applications to cotton-dyeing aniline black is produced in the fibre, by printing the fabric with a mixture of aniline salt and one of the above-mentioned oxidisers, and then developing the dye by steaming at a low temperature.

Aniline black has a relation to the red oxidation product of emeraldin, resembling the relation between emeraldin and quinone monophenyl-di-imine. It cannot be looked upon as a unitary compound. It consists of a mixture varying with the degree of oxidation, a triple or quadruple quinoid combination, to which the following constitutional formulæ are attributed :

I. $C_6H_5N:C_6H_4:NC_6H_4NHC_6H_4NHC_6H_4N:C_6H_4:NC_6H_4N:C_6H_4:NH.$
II. $C_6H_5N:C_6H_4:NC_6H_4N:C_6H_4:NC_6H_4N:C_6H_4:NC_6H_4N:C_6H_4:NH.$

On heating with dilute H_2SO_4, one-eighth of the total nitrogen is split off in the form of ammonia, the imino-group being replaced by oxygen. This is accompanied by an increase in the depth of the colour. These oxygen-bearing substances are contained in aniline black in proportions varying according to the method of preparation. Strong oxidation with chromic acid or lead peroxide and H_2SO_4 converts it almost quantitatively into quinone (B. **42,** 2147, 4118).

Quinone diphenyl-di-imine, *diphenyl-p-azo-phenylene, quinone dianile* $C_6H_4(NC_6H_5)_2$ m.p. 176°–180°, is obtained by the oxidation of diphenyl-amine and diphenyl-p-phenylene-diamine (B. **21,** R. 656). By reduction, quinone dianile passes into diphenyl-p-phenylene-diamine, with which it is related as quinone is to hydroquinone.

Two phenyl-amido-groups may be introduced into the benzene residue of quinone anile and quinone dianile with the same facility as into quinone itself, which, as mentioned before, gives rise to di-anilido-quinone and hydroquinone on boiling its alcoholic solution with aniline. If acetic acid is present (B. **18,** 787), **dianilido-quinone anile** is formed, $(C_6H_5NH)_2C_6H_2(O)(NC_6H_5)$, m.p. 202°, brownish-red needles. This is also formed on heating quinone mono-anil with aniline besides p-oxy-diphenyl-amine (B. **21,** R. 656) and on oxidising aniline with H_2O_2 in a feebly acid solution (B. **15,** 3574).

Dianilido-quinone dianile, *azo-phenin* $(C_6H_5NH)_2C_6H_2(NC_6H_5)_2$, m.p. 241°, garnet-red flakes, results (1) on heating quinone dianile with aniline (B. **21,** R. 656) ; (2) on melting quinone with aniline and aniline chlorohydrate (B. **21,** 683) ; (3) from amido-azo-benzol, p-nitroso-phenol, p-nitroso-diphenyl-amine by the action of aniline (B. **20,** 2480). On heating it is converted into fluorindin (B. **23,** 2791 ; **31,** 1789).

The quinone dianiles are important links in the formation of *indulin* dyes (B. **25,** 2731 ; A. **262,** 247).

Indamines.—These are derived from the indo-anilines by the replacement of the quinone-oxygen atom by the imido- or alkyl-imido-group. They are therefore derivatives of the unknown quinone di-imide, and bear an intimate relation to p-diamido-diphenyl-amine, which is formed by the reduction of the simplest indamine and is the leuco-derivative of the latter.

The *indamines* arise (1) by oxidation, in neutral solution and in the cold, of a mixture of a p-phenylene-diamine with an aniline (Nietzki),

or (2) by the action of nitroso-dimethyl-aniline upon anilines or m-diamines (Witt). They are feeble bases, forming blue- or green-coloured salts with acids; but with an excess of the latter are very easily split up into quinone and the diamine. Because of their instability they find no application, and are only important as intermediate products in the manufacture of thionin and safranin dyestuffs (into which they can be readily transposed). For the relations of the indo-phenols, indanilines, and indamines to the dyes of the *oxazin-*, *thiazin-*, and *diazin*-series—*e.g.* resorufin, methylene blue—the indulins and safranins, see the latter. The simplest indamine is :

Phenylene blue $C_6H_4\begin{cases}N.C_6H_4NH_2\\ \|\\ NH\end{cases}$. This is produced by the oxidation of p-phenylene-diamine with aniline. Its salts are greenish-blue in colour. It yields diamido-diphenyl-amine by reduction. Its tetramethyl derivative is :

Dimethyl-phenylene green $N\begin{cases}C_6H_4.N(CH_3)_2\\ \|\\ C_6H_4.N(CH_3)_2Cl\end{cases}$ (Bindschedler's green).

This is obtained by oxidising dimethyl-paraphenylene-diamine with dimethyl-aniline. Its salts dissolve in water with a beautiful green colour. Its reduction yields tetramethyl-diamido-diphenyl-amine. Digestion with dilute acids resolves it into quinone and dimethyl-amine (B. **16,** 865; **17,** 223). On standing with soda lye, dimethyl-amine splits off and phenol blue is produced; this further separates into quinone phenol-imide (B. **18,** 2915).

Toluylene blue $N\begin{cases}C_6H_4.N(CH_3)_2\\ \|\\ C_7H_5(NH_2).NH\end{cases}$ results from ordinary toluylene-diamine by oxidising it mixed with dimethyl-p-phenylene-diamine, or by the action of HCl-nitroso-dimethyl-aniline. Its salts with one equivalent of acid are of a beautiful blue colour, and are decolorised by an excess of mineral acids with formation of the diacid salts. It is converted into toluylene red on boiling with water.

The genetic connection of the indamines with the indo-anilines and indo-phenol is shown in the possibility of converting the simplest indamine into quinone-aniline-imine, and the latter into quinone-phenol-imine (Möhlau, B. **16,** 2843; **18,** 2915).

Representatives of the indo-phenols, indo-anilines, and indamines containing the naphthalin residue are also known in great numbers, and many, like *naphthol blue* (*q.v.*) or "*indo-phenol,*" have been applied technically (B. **18,** 2916).

On quinoid sulphur compounds, see B. **40,** 3039; **41,** 902.

9. Phenyl-paraffin Alcohols and their Oxidation Products.

In the preceding sections those classes of aromatic hydrocarbons containing one nucleus were described, which resulted from the substitution of the hydrogen atoms of benzene or the benzene residue of the alkyl-benzenes by atoms of other elements or by atomic groups : the *halogen* substitution products, the *nitrogen-containing* derivatives of the benzene hydrocarbons, the aromatic *phosphorus, arsenic, antimony, bismuth, boron, silicon,* and *tin* derivatives, the phenyl *metal*

compounds, the *sulpho-acids* and their relatives, the *phenols*, and the *quinones*.

Attached to these are those classes of bodies formed by the replacement of hydrogen atoms in the side groups of the alkyl-benzols. As in the aliphatic series, the oxygen-containing products are considered the most important. Each class of these derivatives is followed by the corresponding halogen, sulphur, and nitrogen compounds, in which all, or at least a part, of the carbon valences, saturated in the principal compounds by oxygen, are taken up with the elements just named. Prominent among these, as with the aliphatic derivatives, are those bodies in which *one* carbon atom of an alkyl side chain is combined with oxygen :

(1*a*) *The monohydric phenyl-paraffin alcohols and their oxidation products : aldehydes, ketones, carboxylic acids.*

Naturally these compounds, as far as the reactivity of the aliphatic residue is concerned, manifest great similarity to the monohydric aliphatic alcohols and their oxidation products (Vol. I.). This is recalled by their nomenclature and the view that they are phenyl-substitution products of aliphatic substances.

Each of these alkyl-benzene derivatives constitutes a fundamental substance from which, by the replacement of hydrogen atoms of the phenyl residue, as with benzene itself, numerous derivatives can be deduced. In general the benzene substitution products of the *phenyl fatty* bodies, so far as they are worth mention, will be introduced after the corresponding principal bodies. Only the derivatives of monohydric aromatic alcohols, having hydroxyl in their benzene residue, and their oxidation products, which manifest at the same time a phenol character, will be grouped together as :

(1*b*) *Monohydric oxy-phenyl-paraffin alcohols and their oxidation products.*

Then will follow (2) *polyhydric phenyl-paraffin alcohols, in which but one hydroxyl group is joined to a side chain, and their oxidation products.* The conclusion of this section will be (3) *polyhydric phenyl-paraffin alcohols, in which more than one hydroxyl group is attached to a side chain, and their oxidation products.*

In the subsequent sections the mononuclear derivatives with unsaturated side chains will be summarised.

(*a*) Monohydric Phenyl-paraffin Alcohols and their Oxidation Products.

1. **Monohydric Phenyl-paraffin Alcohols.**—The true alcohols of the benzene series are produced by the entrance of an hydroxyl group into the side chain of an alkyl-benzol,—*primary*, *secondary*, and *tertiary*. The primary alcohols, upon oxidation, yield *aldehydes* and *acids*. The secondary change to *ketones* :

Benzyl alcohol $C_6H_5CH_2OH$	Phenyl-methyl-carbinol $C_6H_5CH(OH)CH_3$
↓ Benzaldehyde C_6H_5CHO	↓ Acetophenone . . $C_6H_5COCH_3$.
↓ Benzoic acid C_6H_5COOH.	

Formation.—The similarity of benzyl alcohol and its homologues to ethyl alcohol finds expression at the very outset in the methods of

producing both classes :—(1) by saponification of alkyl-benzols containing an halogen atom in the side chain—the haloid acid esters of the benzyl alcohols—*e.g.* benzyl chloride with water alone (A. **196**, 353), with water and lead oxide (A. **148**, 81), or with potashes. Benzyl alcohols are also produced by converting the chlorides into acetates and saponifying the latter.

(2) By the action of nitrous acid upon primary amines, the reduction products of aromatic acid nitriles—*e.g.* cumo- and hemimelli-benzyl alcohol.

(3) By the action of nascent hydrogen on the corresponding aldehydes and ketones.

(4) The phenyl-paraffin alcohols are obtained from the aromatic aldehydes by treating with alcoholic or aqueous potash. This reaction, in which the corresponding carboxylic acids are also formed, occurs only exceptionally in the paraffin aldehydes (B. **14**, 2394 ; C. 1902, I. 1212) ; from two molecules benzaldehyde, benzyl alcohol and potassium benzoate are produced, benzoic benzyl ester being probably an intermediate product (C. 1899, II. 1111) :

$$2C_6H_5CHO \longrightarrow C_6H_5COOCH_2C_6H_5 \xrightarrow{KOH} C_6H_5COOK + C_6H_5CH_2OH.$$

(5*a*) From the aromatic carboxylic acids or their esters by electrolytic reduction in alcoholic sulphuric-acid solution, with great excess of cathode voltage. The reduction of the acid esters leads simultaneously to the formation of the corresponding ethers ; benzoic methyl ester gives benzyl alcohol and benzyl-methyl ether $C_6H_5CH_2OCH_3$ (B. **38**, 1745 ; **39**, 2933 ; C. 1908, II. 1863).

(5*b*) From the esters of the phenyl fatty acids (except benzoic acid) by reduction with sodium and alcohol (German patent 164,294).

(5*c*) By reducing amides of aromatic carboxylic acids, containing the carboxylic group attached to the benzene nucleus, with sodium amalgam in acid solution (B. **24**, 173).

(6) By the reduction of unsaturated alcohols. Cinnamyl alcohol $C_6H_5CH=CH.CH_2OH$ becomes hydro-cinnamyl alcohol $C_6H_5.CH_2.CH_2.CH_2OH$ (see Allyl Alcohol).

(7) They are formed in the nuclear synthesis by the action of metallic alkylates upon aldehydes, ketones, acid esters or acid chlorides, and halogen hydrins. Thus (*a*) phenyl-magnesium bromide and acetone yield phenyl-dimethyl-carbinol $C_6H_5C(OH)(CH_3)_2$; (*b*) aromatic aldehydes, ketones, acid esters, or chlorides with zinc alkyls, and especially magnesium-alkyl haloids (Vol. I.), give secondary and tertiary phenyl-paraffin alcohols, the latter easily losing water, and passing into olefin benzols (C. 1901, I. 1357 ; II. 623 ; B. **35**, 2633) ; (*c*) phenyl-magnesium bromide and ethylene chlorohydrin yield phenyl-ethyl alcohol $C_6H_5CH_2CH_2OH$ (C. 1907, I. 1033).

Benzyl alcohol, *phenyl-carbinol* [*phenyl-methylol*] $C_6H_5CH_2OH$, m.p. 206°, with specific gravity 1·062 (0°), is isomeric with the cresols. It occurs as benzoic ester and benzyl-cinnamic ester in the balsams of *Peru* and *Tolu*, and in *storax* (A. **169**, 289) ; as an acetic ester, and sometimes free in certain etheric oils, *e.g.* the oil of jasmine flowers (B. **32**, 567).

It is produced by the methods (1), (2), (3), (4), (5*a*), and (5*c*), given

above, from benzaldehyde, benzyl chloride, benzoic acid, and benzamide. Reactions (1) and (3) are used as methods of preparation. It is a colourless liquid, with a faint aromatic odour. It dissolves with difficulty in water, but readily in alcohol and ether. It yields benzaldehyde and benzoic acid when oxidised. On heating with hydrochloric acid or hydrobromic acid, the OH group is replaced by halogens. Benzoic acid and toluol result on distilling it with concentrated potash.

History.—As early as 1832 Liebig and Wöhler, in the course of their celebrated investigation upon the radical benzoyl, obtained this alcohol as the result of the interaction of alcoholic potash and benzaldehyde (A. **3**, 254, 261). Cannizzaro (1853) was the first to discover the alcohol in studying this reaction.

Homologous Phenyl-paraffin Alcohols.—The primary alcohols are chiefly made by methods (1), (2), (3), (4), (5*a*), (5*b*), (5*c*), and (7*c*); hydro-cinnamyl alcohol by method (6); the secondary alcohols by method (1), or by the reduction of the ketones according to method (3), and the tertiary alcohols, like benzyl-dimethyl carbinol, by method (7).

Nucleus homologous benzyl alcohols :

		M.p.	B.p.	
o-Tolyl carbinol .	$CH_3[2]C_6H_4[1]CH_2OH$	34°	223°	(B. **24**, 174)
m-Tolyl carbinol .	$CH_3[3]C_6H_4[1]CH_2OH$	liquid	217°	(B. **18**, R. 66)
p-Tolyl carbinol .	$CH_3[4]C_6H_4[1]CH_2.OH$	59°	217°	(A. **124**, 255)
2, 4-Dimethyl-benzyl alcohol . .	$(CH_3)_2[2, 4]C_6H_3[1]CH_2.OH$	22°	232°	(B. **21**, 3085)
3, 5-Mesityl alcohol .	$(CH_3)_3[3, 5]C_6H_2[1]CH_2.OH$	liquid	220°	(B. **16**, 1577)
2, 4, 5-Cumo-benzyl alcohol . .	$(CH_3)_3[2,4,5]C_6H_2[1]CH_2.OH$	168°	..	(B. **24**, 2411)
3, 4, 5-Hemimelli-benzyl alcohol . .	$(CH_3)_3[3,4,5]C_6H_2[1]CH_2.OH$	78°	..	(B. **24**, 2411)
Mellithyl alcohol	$(CH_3)_5C_6.CH_2OH$	160°	..	(B. **22**, 1217)
p-Cumin alcohol .	$(CH_3)_2CH[4]C_6H_4[1]CH_2.OH$	..	246°.	

Other homologues are the *phenyl-ether alcohols* :

Benzyl carbinol $C_6H_5CH_2.CH_2OH$, *β-phenyl-ethyl alcohol*, a main constituent of the etheric oil of roses (B. **34**, 2803), boils at 219° (B. **9**, 373).

Phenyl-methyl carbinol $C_6H_5.CH(OH)CH_3$ boils at 203°, from benzaldehyde and CH_3MgI (C. 1901, II. 623).

o-, m-, and p-tolyl-ethyl alcohol $CH_3C_6H_4CH_2CH_2OH$, b.p. 243·5°, 243°, and 245°, from the tolyl-magnesium bromides with ethylene chlorohydrin (C. 1907, I. 1033), or by electrolytic reduction of the three isomeric tolyl-acetic acids (C. 1908, II. 1863).

Phenyl-propyl Alcohols.—Hydro-cinnamyl alcohol $C_6H_5.CH_2.CH_2.CH_2OH$ boils at 235°. It is obtained from its cinnamic acid ester, which is present in *storax* (A. **188**, 202). **Benzyl-methyl carbinol** $C_6H_5.CH_2.CH(OH).CH_3$ boils at 215°. **Phenyl-ethyl carbinol** $C_6H_5CH(OH)CH_2CH_3$, b.p. 221°, obtained like phenyl-propyl.

Phenyl-iso-propyl, phenyl-iso-butyl, and **phenyl-iso-amyl carbinol,** $b.p._{10}$ 114°, $b.p._{15}$ 113°, $b.p._9$ 122° and $b.p._8$ 132° respectively, from benzaldehyde, with the corresponding alkyl-magnesium iodides (C. 1901, II. 623).

Phenyl-dimethyl carbinol $C_6H_5C(OH)(CH_3)_2$, m.p. 23°, $b.p._{10}$ 94°,

is obtained from phenyl-magnesium bromide with acetones, or from aceto-phenone and benzoic methyl ester with magnesium-methyl iodide. **Benzyl-dimethyl carbinol** $C_6H_5.CH_2.C(OH)(CH_3)_2$, m.p. 21°, b.p. 225°. For further dialkyl-benzyl carbinols, see C. 1904, I. 1496.

DERIVATIVES OF THE PHENYL-PARAFFIN ALCOHOLS.—*Haloid Esters.*—Benzyl chloride and benzyl bromide are produced when chlorine or bromine acts upon boiling toluol (Beilstein, A. **143**, 369). The action is favoured by sunlight (C. 1898, I. 1019). Benzyl chloride, bromide, and iodide are also formed from benzyl alcohol and the haloid acids, and benzyl iodide by the action of potassium iodide upon benzyl chloride (A. **224**, 126) :

Benzyl chloride .	. $C_6H_5.CH_2Cl$	liquid	b.p. 176°
Benzyl bromide .	. $C_6H_5.CH_2Br$	,,	,, 210°
Benzyl iodide .	. $C_6H_5.CH_2I$	melts at 24° and decomposes.	

Benzyl chloride, isomeric with the three chloro-toluols, is an important reagent, by means of which numerous derivatives of benzyl alcohol have been prepared, as its chlorine atom is readily exchanged. It passes into benzyl alcohol when boiled with water. Heated with water and lead nitrate it yields benzaldehyde, and by oxidation benzoic acid :

$$C_6H_5CH_3 \longrightarrow C_6H_5.CH_2Cl \begin{cases} \longrightarrow C_6H_5.CH_2OH \\ \longrightarrow C_6H_5.CHO \longrightarrow C_6H_5COOH. \end{cases}$$

The following *ethers* have been made by the action of sodium alcoholates upon benzyl chloride, or by electrolytic reduction of benzoic esters (B. **38**, 1752). *Benzyl-methyl ether* boils at 168°, obtained from phenyl-magnesium bromide and monochloro-methyl ether (C. 1908, I. 716). The *ethyl ether* boils at 185°. The *benzyl ether* (A. **241**, 374) $(C_6H_5CH_2)_2O$, boiling at 296°, results from the action of boron trioxide upon benzyl alcohol. **Methylene-dibenzyl ether** $CH_2(OCH_2.C_6H_5)_2$ (A. **240**, 200). **Benzyl-arabinoside** $C_5H_9O_5.CH_2.C_6H_5$ melts at 172° (B. **27**, 2482). *Benzyl-phenyl ether* melts at 39° and boils at 287°.

Homologous Phenyl-alkyl Chlorides.—**α-Chlorethyl benzol** $C_6H_5CHCl.CH_3$ boils at 194°; cp. B. **39**, 2209. **(ω-) β-Chlorethyl benzol** $C_6H_5.CH_2.CH_2Cl$, boils at 93° (17 mm.). **o-, m-, p-Methyl-benzyl chloride** $CH_3.C_6H_4CH_2Cl$ boil at 198°, 195°, and 192° respectively. **α-Chloro-propyl benzol** $C_6H_5.CHCl.CH_2.CH_3$ and **β-chloro-propyl benzol** $C_6H_5.CH_2CHClCH_3$ boil about 203°–207°, with the splitting off of hydrochloric acid and the production of **α-phenyl-propylene** $C_6H_5.CH:CH.CH_3$ and **allyl benzol** $C_6H_5CH_2CH=CH_2$ **ω-Bromo-propyl benzol** $C_6H_5CH_2.CH_2.CH_2Br$, $b.p._{11}$ 109° (B. **48**, 178).

Benzyl phosphates: the *mono-* melts at 78°, the *di-* is liquid, and the *tri-* melts at 64° (A. **262**, 211). **Benzyl-sulphuric acid** $C_6H_5CH_2.OSO_3H$, formed besides dibenzyl formal $CH_2(OCH_2C_6H_5)_2$ from benzyl alcohol and methylene sulphate $SO_4:CH_2$ (C. 1900, I. 101, 249). **Benzyl nitrite** $C_6H_5CH_2ONO$, $b.p._{35}$ 81°, from benzyl alcohol and HNO_2 in aqueous solution (B. **34**, 755).

Esters of Carboxylic Acid.—Benzyl acetate $C_6H_5CH_2.O.CO.CH_3$, b.p. 216°. The action of sodium upon the benzyl esters of the fatty acids is peculiar, and tends to the formation of benzyl esters of higher phenyl fatty acids (*q.v.*). Benzyl acetate yields phenyl-propionic benzyl ester.

Dibenzyl oxalate $(C_6H_5.CH_2O.CO)_2$ melts at 80°.

SULPHUR DERIVATIVES OF BENZYL ALCOHOL are formed just like the sulphur compounds of the fatty alcohols.

Benzyl sulphydrate, *benzyl mercaptan* $C_6H_5.CH_2.SH$. It is a liquid with a leek-like odour; boils at 194°, and at 20° has a specific gravity =1·058 (A. **140,** 86).

Benzyl disulphide $(C_6H_5CH_2)_2S_2$, m.p. 71° (B. **20,** 15), results from the oxidation of benzyl sulphydrate in the air (A. **136,** 86). Also from sodium-benzyl hyposulphite by electrolysis (C. 1908, I. 1173), or by the action of iodine (C. 1909, II. 1739).

Benzyl sulphide $(C_6H_5.CH_2)_2S$, m.p. 49°, when subjected to dry distillation yields *stilbene* (q.v.), *stilbene sulphide, dibenzyl* (q.v.), *thionessal* or *tetraphenyl-thiophene* (q.v.), and toluol. The **sulphone** $(C_6H_5.CH_2)_2SO_2$, m.p. 150°. It results when the sulphoxide in glacial acetic acid is acted upon by $KMnO_4$ (B. **13,** 1284; **36,** 534).

Benzyl-dimethyl-sulphine iodide $C_6H_5CH_2S(CH_3)_2I$ is an orange-red coloured compound (B. **7,** 1274).

Tribenzyl-sulphinic chloride $(C_6H_5CH_2)_2SCl$. The ferric chloride double salt is obtained in the form of light-green flakes, of m.p. 98°, by the action of ferric chloride upon an etheric solution of benzyl chloride and benzyl sulphide. **Tribenzyl-sulphinic iodide,** m.p. 75° (B. **40,** 4932).

Benzyl sulphoxide $(C_6H_5CH_2)_2SO$, m.p. 133°, is formed by oxidising benzyl sulphide with nitric acid (B. **13,** 1284). **Benzyl sulphone** $(C_6H_5CH_2)_2SO_2$, m.p. 150°, from benzyl sulphoxide with MnO_4K in glacial acetic acid (B. **13,** 1284). **Benzyl disulphoxide** $C_6H_5CH_2SOSOCH_2C_6H_5$, m.p. 108°, from benzyl disulphide and H_2O_2.

Methyl- and **ethyl-benzyl sulphone,** m.p. 127° and 84°, from sodium-benzyl sulphinate and CH_3I and C_2H_5I respectively (B. **39,** 3315).

Benzyl-sulphinic acid $C_6H_5CH_2SO_2H$, obtained by the reduction of benzyl sulpho-chloride. It easily splits into benzaldehyde and sulphurous acid (B. **39,** 3308).

Benzyl-sulphonic acid $C_6H_5.CH_2.SO_3H$ is a deliquescent crystalline mass; it is isomeric with toluol-sulphonic acid. The potassium salt is formed on boiling benzyl chloride with potassium sulphite. The chloride melts at 92° (B. **13,** 1287).

Benzyl-hyposulphurous acid $C_6H_5CH_2SSO_3H$, m.p. 74° (B. **23,** R. 284).

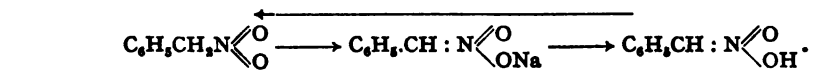
NITROGEN DERIVATIVES OF THE PHENYL-PARAFFIN ALCOHOLS.

PHENYL-NITRO-PARAFFINS.—When the homologous benzols are heated in sealed tubes with dilute nitric acid, the nitro-groups usually enter the side chains with the formation of phenyl-nitro-paraffins (Konowaloff, B. **28,** 1850, R. 235; **29,** 2199; C. 1899, I. 1237).

By this treatment toluol yields **phenyl-nitro-methane** $C_6H_5.CH_2.NO_2$. This body has also been prepared from nitro-benzal-phthalide, as well as from benzyl haloids, but best from the iodide (B. **29,** 700) by the action of silver nitrite. It is an oil, boiling with decomposition at 226°. It is most easily obtained from phenyl-nitro-aceto-nitrile $C_6H_5CH(NO_2)CN$ (*q.v.*) by boiling with NaHO, or by the action of ethyl nitrate and potassium ethylate upon phenyl-acetic ester, a reaction

in which the carbox-ethyl group is split off in the form of carbonic acid ester (B. **42**, 1930). On heating with NaHO to 160° the phenyl-nitro-methane is further changed, nitrogen oxides being split off and stilbene formed (B. **36**, 1194; **38**, 502).

Phenyl-nitro-methane dissolves, like the nitro-paraffins (Vol. I.), in sodium hydroxide, forming a sodium salt, from which the oily phenyl-nitro-methane is regained by the action of CO_2 or acetic acid. If, however, the sodium salt be precipitated with mineral acids, a crystalline substance, m.p. 84°, is obtained. This is isomeric with the oily body, and is distinguished from it by the red coloration it yields with ferric chloride, as well as by its electric conductivity. It quickly changes, both in solution and when in a free state, into the oily isomeride. Its constitution certainly corresponds to the formula adopted for the sodium salts of the nitro-paraffins, from which, however, the corresponding free bodies in the fatty series have not been successfully isolated (Hantzsch and O. W. Schultze, B. **29**, 2251):



Similar stable and unstable isomerides have also been obtained from the nucleus homologues and substituted phenyl-nitro-paraffins (B. **29**, 2193, 2253, R. 40).

The action of acid chlorides upon the sodium salts of the phenyl-nitro-methanes usually gives acyl derivatives of benzo-hydroxamic acid, in consequence of an intramolecular oxidation process; sodium phenyl-nitro-methane and acetyl chloride give **aceto-benzo-hydroxamic acid** $C_6H_5C(OCOCH_3)NOH$ (C. 1900, I. 177). On ammonium salts of phenyl-nitro-methane, see C. 1900, I. 1092.

Tolyl-nitro-methane, see B. **38**, 503; C. 1905, II. 817. ω-Nitro-durol $(CH_3)_3[2, 4, 5]C_6H_2[1]CH_2NO_2$, m.p. 52°; iso-nitro-compound, m.p. 102°–106°, is easily obtained by nitrogenation of durol with benzoyl nitrate (B. **42**, 4154).

Phenyl-methyl-nitro-methane $C_6H_5CH(CH_3)NO_2$, b.p. 115°, from aceto-phenone monoxime (*q.v.*) by oxidation with Caro's acid; the corresponding unstable nitronic acid $C_6H_5C(CH_3)$: NOOH melts about 45° (B. **36**, 706).

Phenyl-paraffin Amines, Benzyl-amines.—(1) Alcoholic ammonia converts benzyl chloride into *mono-*, *di-*, and *tribenzyl-amines* (B. **28**, 2971; C. 1901, II. 1155).

Most of the other methods of producing benzyl-amine are reactions which have been fully discussed in connection with the primary alkyl-amines.

Benzyl-amine is formed (2) by the reduction of phenyl-nitro-methane, benzaldoxime, and benzylidene-phenyl-hydrazone (B. **19**, 1928; **35**, 1513; **42**, 1559); (3) and (4) by heating benzaldehyde with ammonium formate or formamide (B. **19**, 2128; **20**, 104; A. **343**, 54), together with di- and tribenzyl-amine; (5) by the reduction of benzo-nitrile (B. **20**, 1709) and (6) of benzo-thiamide (B. **21**, 51); (7) of benzamide (C. 1899, II. 623); (8) by saponifying benzyl iso-cyanide or benzyl carbon-imide $C_6H_5CH_2NCO$ (B. **5**, 692), and (9) benzyl acetamide $C_6H_5CH_2NHCOCH_3$ (B. **12**, 1297); (10) by the distillation of the

phenyl-amido-acetic acid $C_6H_5CH(NH_2)CO_2H$ (B. **14**, 1969); and (11) by the action of caustic alkali and bromine upon phenyl-acetic amide. Benzyl-amine is a liquid, dissolving readily in water. It differs from its isomeric toluidin in being a strong base, which attracts CO_2 from the air.

Caro's acid oxidises benzyl-amine to benzaldoxime, phenyl-nitro-methane, and benzo-hydroxamic acid, besides benzaldehyde and benzoic acid (B. **34**, 2262).

Dibenzyl-amine $(C_6H_5CH_2)_2NH$, b.p. 300°, is also obtained from benzalazin $C_6H_5CH : N.N : CHC_6H_5$ by reduction with zinc dust and acetic acid, and (with benzyl-amine) by reduction of benzo-nitrile.

Nitroso-dibenzyl-amine $(C_6H_5CH_2)_2NNO$, m.p. 61° (B. **34**, 557).

Tribenzyl-amine $(C_6H_5CH_2)_3N$, m.p. 91°.

Homologous benzyl-amines are isomeric with corresponding alphyl-amines. They are mostly formed by reducing nitriles with alcohol and sodium; some by the reduction of oximes or nitro-compounds, while others are obtained by the methods indicated under benzyl-amine.

β-Phenyl-ethyl-amine	$C_6H_5CH_2CH_2NH_2$	b.p.	197° [1]
α-Phenyl-ethyl-amine	$C_6H_5CH(NH_2)CH_3$	,,	187° [2]
γ-Phenyl-propyl-amine	$C_6H_5.CH_2.CH_2CH_2NH_2$	,,	221° [3]
β-Phenyl-propyl-amine	$C_6H_5CH(CH_3).CH_2NH_2$	,,	210° [4]
α-Phenyl-propyl-amine	$C_6H_5CH(NH_2).CH_2.CH_3$	,,	205°
β-Phenyl-iso-propyl-amine	$C_6H_5CH_2.CH(NH_2)CH_3$	,,	203° [5]
o-Tolu-benzyl-amine	$CH_3[2]C_6H_4[1]CH_2NH_2$	,,	205° [6]
m-Tolu-benzyl-amine	$CH_3[3]C_6H_4[1]CH_2NH_2$	,,	201° [7]
p-Tolu-benzyl-amine	$CH_3[4]C_6H_4[1]CH_2NH_2$	,,	195° [8]
ω-Pseudo-cumyl-amine	$(CH_3)_2[2, 4]C_6H_3[1]CH_2NH_2$	,,	218° [9]
ω-Mesityl-amine	$(CH_3)_2[3, 5]C_6H_3[1]CH_2NH_2$	,,	221° [10]
ω-Duryl-amine	$(CH_3)_2[2, 4, 5]C_6H_2[1]CH_2NH_2$	m.p.	52° [11]
Cumyl-amine	$(CH_3)_2CH[4]C_6H_4[1]CH_2NH_2$	b.p.	226° [12]
Cumo-benzyl-amine	$(CH_3)_2[2, 4, 5]C_6H_2[1]CH_2NH_2$	m.p.	64° [13]
Hemimelli-benzyl-amine	$(CH_3)_2]3, 4, 5]C_6H_2[1]CH_2NH_2$	,,	123° [14]

Literature.—[1] B. **26**, 1904; [2] B. **27**, 2306; [3] B. **27**, 2309; [4] B. **26**, 2875; [5] B **20**, 618; [6] B. **23**, 1026; **33**, 1013; C. 1899, I. 1238; [7] B. **23**, 3165; [8] B. **20**, 1719; [9] B. **21**, 3083; [10] C. 1899, I. 1238; [11] B. **42**, 4156; [12] B. **20**, 2414; [13] B. **24**, 2409; [14] B. **24**, 2411.

α-Phenyl-ethyl-amine $C_6H_5CH(NH_2)CH_3$ is obtained by electrolytic reduction of aceto-phenone oxime (B. **35**, 1515); it contains an unsymmetrical C atom, and has been split up into its optically active components by means of its maleïc salt (C. 1899, II. 1123; 1905, II. 1583).

The pure benzyl-amines are associated with benzyl-alkyl- and benzyl-aryl-amines, as well as benzyl-alkyl-ammonium compounds. Benzyl-alkyl-amines, like **benzyl-ethyl-amine** $C_6H_5.CH_2NHC_2H_5$, and **cumyl-ethyl-amine** $C_3H_7C_6H_4CH_2NHC_2H_5$, are obtained from the corresponding benzylidene-alkyl-amines by reduction with Na and alcohol, or by heating benzaldehyde with organic formates (B. **35**, 410; A. **343**, 54). **Dibenzyl-ethylene-diamine** $(C_6H_5CH_2NH)_2C_2H_4$, b.p. 175°–182°, from dibenzylidene-ethylene-diamine; it condenses with ethylene bromide to dibenzyl-piperazin (C. 1898, II. 743). **Pheno-propyl-methyl-amine** $C_6H_5CH_2CH_2CH_2NHCH_3$, $b.p._{18}$ 134°, is obtained from cin-

namylidene-methyl-amine $C_6H_5CH:CH.CH:NCH_3$ with sodium and alcohol (C. 1902, I. 662). **α-Phenyl-ethyl-methyl-amine** $C_6H_5(CH_3)CHNHCH_3$, b.p.$_{13}$ 87°, and **α-phenyl-propyl-methyl-amine**, b.p.$_{20}$ 96°, are obtained by the action of methyl- and ethyl-magnesium iodide respectively upon benzal-methyl-amine (*J. pr. Ch.* 2, **77**, 20).

Benzyl-phenyl-allyl-methyl-ammonium iodide $(C_6H_5CH_2)(C_6H_5)(C_3H_5)(CH_3)NI$ contains an unsymmetrical N atom, and has been split up into optically active components by means of campho-sulphonic acid (B. **32**, 3561; C. 1901, II. 206). Similarly, the splitting up of many other quaternary benzyl-ammonium compounds, with four different radicles, has been accomplished (see E. Wedekind, *Stereo-chemistry of Quinquevalent Nitrogen*, Leipzig, 1907).

Benzyl-aniline $C_6H_5.CH_2.NH.C_6H_5$ melts at 32°, and is formed from aniline and benzyl chloride (A. **138**, 225), or by the reduction of benzylidene-aniline with sodium in alcoholic solution (A. **241**, 330), or by electrolytic reduction (B. **42**, 3460). When heated to 220° with sulphur it yields *thio-benzanilide*, and *benzenyl-amido-thio-phenol* at 250° (A. **259**, 300). For acid derivatives of benzyl-aniline, see B. **32**, 2672.

Dibenzyl-aniline $(C_6H_5.CH_2)_2.N.C_6H_5$, m.p. 67° (B. **20**, 1611).

C-alkyl-benzyl-anilines like $C_6H_5CH(CH_3)NHC_6H_5$ are produced by the attachment of alkyl-magnesium haloids to benzal-aniline:

$$C_6H_5CH:NC_6H_5 \xrightarrow{CH_3.MgI} C_6H_5CH(CH_3).N(MgI)C_6H_5 \xrightarrow{H_2O} C_6H_5CH(CH_3)NHC_6H_5.$$

The chlorohydrates of these bases, when heated to 220° with aniline chlorohydrate, undergo an atomic displacement analogous to Hofmann's transposition, with formation of C-alkyl-p-amido-diphenyl-methanes, *e.g.*

$$C_6H_5CH(CH_3)NHC_6H_5 \longrightarrow NH_2C_6H_4CH(CH_3)C_6H_5.$$

C-Methyl-, -ethyl-, -propyl-, and **-amyl-benzyl-aniline**, b.p.$_{20}$ 183°, 192°, 200°, and 215° (B. **38**, 1761).

Benzyl-oxethyl-amine $C_6H_5.CH_2.NH.CH_2.CH_2OH$, *picrate*, melting at 136°, results from the rupture of the phenyl-oxazolin ring $C_6H_5.C\begin{matrix}O—CH_2\\ \diagdown\\ N—CH_2\end{matrix}$ by sodium and alcohol (B. **29**, 2382).

The following representatives of the numerous benzylated acid amides and benzylated nitrogen derivatives of carbonic acid may be mentioned:

Benzyl acetamide $C_6H_5CH_2NHCOCH_3$, m.p. 60° (B. **19**, 1286). Its nitroso-derivative $C_6H_5CH_2N(NO)COCH_3$ is decomposed by alcohols with elimination of nitrogen, and formation of benzyl-alkyl ethers; this decomposition, recalling the diazo-bodies, is also shown by other nitrosated acid derivatives of benzyl-amine (B. **31**, 2640; **32**, 78).

Dibenzyl-urea chloride $(C_6H_5CH_2)_2NCOCl$ is an oil (B. **25**, 1819). **Benzyl-urethane** $C_6H_5CH_2NHCO_2C_2H_5$, m.p. 44°.

Benzyl-urea $C_6H_5CH_2NHCONH_2$, m.p. 147°. Sym. and unsym. **di-benzyl-urea** melt at 167° and 124° (B. **9**, 81). **Tri-** and **tetrabenzyl-urea** melt at 119° and 85° (B. **25**, 1826).

Benzyl-thio-urea melts at 164° (B. **24**, 2727; **25**, 817).

Dibenzyl-guanidin $(C_6H_5CH_2NH)_2C:NH$, m.p. 100° (B. **5**, 695).

Benzyl iso-cyanate, *benzyl carbonimide* $C_6H_5CH_2N:CO$, is a liquid with a penetrating odour. **Benzyl cyanurate** melts at 157° (B. **5**, 692).

Benzyl-mustard oil $C_6H_5CH_2N : CS$, b.p. 243°, forms the chief ingredient of the ethereal oils of various cresses (B. **32**, 2336).

BENZYL-HYDRAZINS.—**Benzyl-hydrazin** $C_6H_5CH_2NH.NH_2$, b.p.$_{41}$ 103°, is obtained by decomposition of its benzylidene compound $C_6H_5CH_2NH.N : CHC_6H_5$ with acids. This compound is obtained by a partial reduction of benzal-azin with Na amalgam and alcohol. With HNO_2, benzyl-hydrazin gives a very stable nitroso-compound $C_6H_5CH_2N(NO)NH_2$, m.p. 71° (B. **33**, 2736).

Unsym. **dibenzyl-hydrazin** $(C_6H_5CH_2)_2N.NH_2$, m.p. 65°, from benzyl chloride with hydrazin hydrate; also from dibenzyl nitrosamine by reduction with zinc dust and acetic acid; by oxidation with HgO it yields a tetrazone, m.p. 97°; but under other conditions nitrogen seems to be liberated, with the formation of dibenzyl (B. **33**, 2701; **34**, 552).

Sym. **benzyl-phenyl-hydrazin** $C_6H_5CH_2NHNHC_6H_5$, m.p. 35°, b.p. about 290°, is obtained by the reduction of benzal-phenyl-hydrazone with Na amalgam in alkaline solution. Oxidation in air readily reconverts it into the phenyl-hydrazone (*J. pr. Ch.* **2**, **78**, 49). Unsym. **benzyl-phenyl-hydrazin** $C_6H_5CH_2N(C_6H_5)NH_2$, m.p. 26°, from phenyl-hydrazin and benzyl chloride, is suitable for separating sugars in the form of hydrazones (B. **32**, 3234; C. 1904, II. 1293). On oxidation it passes into **dibenzyl-diphenyl-tetrazone** $C_6H_5CH_2(C_6H_5)N.N : N.N(C_6H_5)CH_2C_6H_5$, m.p. 145°, which on heating in xylene solution decomposes into Na and sym. dibenzyl-diphenyl-hydrazin, b.p.$_{22}$ 181° (B. **39**, 2566).

BENZYL-DIAZO-COMPOUNDS. BENZYL-TRIAZENES. BENZYL-AZIDES.

Potassium-benzyl diazotate $C_6H_5CH_2N : NOK$ (?) is obtained by the action of highly concentrated potash lye upon **nitroso-benzyl-urethane** $C_6H_5CH_2N(NO)CO_2C_2H_5$. It forms a white crystalline powder, which, on wetting with water, splits up into KOH and **phenyl-diazo-methane** $C_6H_5CH\langle{}^{N}_{N}\rangle$; the latter is a reddish-brown oil, which, on distillation, breaks up into nitrogen and **stilbene** $C_6H_5CH : CHC_6H_5$; on warming with water, into N_2 and benzyl alcohol; with alcohol, into N_2 and benzyl ether; and with HCl, into N_2 and benzyl chloride (B. **35**, 903; cp. also Diazo-methane, Vol. I.).

Sodium-benzyl iso-azotate $C_6H_5CH_2.N : NONa$, colourless needles, is formed by the action of ethyl nitrite and sodium methylate upon unsym. nitroso-phenyl-hydrazin, with simultaneous liberation of nitrous oxide. It differs decidedly from the corresponding K salt. In cold water it dissolves unchanged, but on heating, or with dilute acids, it decomposes into N_2 and benzyl alcohol. On reduction it passes into benzyl-hydrazin; on oxidation, into **benzyl-nitramine** $C_6H_5CH_2NHNO_2$ m.p. 39°, from which it may be recovered by reduction with aluminium and soda (A. **376**, 255).

Benzyl-methyl-triazene $C_6H_5CH_2N : N.NHCH_3$, a colourless oil, resembling in its instability the aliphatic diazo-amido-compounds (Vol. I.), and readily decomposed even by CO_2. Obtained from benzyl azide and CH_3MgI. The **cupro-salt** melts at 114°, and consists of pale-yellow grains; **silver salt**, m.p. 125°, colourless needles (B. **38**, 684).

Benzyl-phenyl-triazene $C_6H_5CH_2NH.N:NC_6H_5$ or $C_6H_5CH_2N:N.NHC_6H_5$, m.p. 75°, colourless flakes, is obtained by transforming benzyl azide with C_6H_5MgBr, or phenyl azide with $C_6H_5CH_2MgCl$. Dilute HCl splits it up into benzyl chloride, aniline chlorohydrate, and nitrogen (B. **38,** 682).

Benzyl-azide $C_6H_5CH_2N\langle^{N}_{N}$, b.p.$_{11}$ 74°, from $C_6H_5CH_2N\langle^{NH_2}_{NO}$, benzyl-nitroso-hydrazin, on boiling with dilute H_2SO_4, or from benzyl iodide with silver nitride, is a very stable ether of nitro-hydric acid; it is only decomposed by fairly concentrated H_2SO_4, yielding, with liberation of N, (1) benzaldehyde and NH_3; (2) formaldehyde and aniline; (3) benzyl-amine and N_2O (?); or (4) benzyl alcohol (and NH_3) (*J. pr. Ch.* 2, **68,** 428; **B. 35,** 3229).

Benzyl-hydroxylamines.—**α-Benzyl-hydroxylamine,** b.p.$_{50}$ 123°, best obtained by splitting up benzyl acetoxime $C_6H_5CH_2ON:C(CH_3)_2$ with HCl; in a similar manner α, **p-chloro-benzyl-hydroxylamine,** m.p. 38°, b.p.$_{17}$ 128°, and α, **p-bromo-benzyl-hydroxylamine,** m.p. 37°, b.p.$_{10}$ 133°, have been prepared. The α-benzyl-hydroxylamine, on heating in a pressure tube, breaks up, partly into NH_3, water, and benzal-doxime-benzyl ether. With $SOCl_2$ it yields **thionyl-benzyl-hydroxyl-amine** $C_6H_5CH_2ON:SO$, b.p.$_{50}$ 154°; with $COCl_2$, **dibenzyl-oxy-urea** $(C_6H_5CH_2ONH)_2CO$, m.p. 88°; with formimido-ether chlorohydrate, **dibenzyl-formo-hydroxamoxime** $C_6H_5CH_2ONH.CH:NOCH_2C_6H_5$, m.p. 42° (B. **26,** 2155; **38,** 1975). Treated with benzyl chloride, the α-benzyl-hydroxylamine passes into **αβ-dibenzyl-hydroxylamine** $C_6H_5CH_2O.NHCH_2C_6H_5$, a liquid, and **tribenzyl-hydroxylamine** $C_6H_5CH_2ON(CH_2C_6H_5)_2$, liquid. The former, split up with HCl, gives **β-benzyl-hydroxylamine** $C_6H_5CH_2.NHOH$, m.p. 57°, which, with benzyl chloride, yields **β-dibenzyl-hydroxylamine** $(C_6H_5CH_2)_2NOH$, m.p. 123° (A. **275,** 133). The β-benzyl-hydroxylamine combines with aldehydes to form N-benzyl-aldoximes. With oxidisers, like bromine water or chromic acid, it is converted mainly into bis-nitroso-benzyl $(C_6H_5CH_2NO)_2$. The latter is converted by HCl into benzal-benzoyl-hydrazin and its disintegration product:

$$(C_6H_5CH_2NO)_2 \longrightarrow C_6H_5CH:N.NHCOC_6H_5+H_2O.$$

Atmospheric oxygen produces mainly benzaldoxime (B. **38,** 3193; A. **328,** 265). Oxidation of the β-dibenzyl-hydroxylamine produces N-benzyl-benzaldoxime.

Substituted benzyl alcohols are derived from substituted benzyl chlorides when they are heated with aqueous potash (B. **25,** 3290), or by means of acetic esters. Many, like m-nitro-benzyl alcohol, are also obtained by the action of alcoholic potash upon the corresponding aldehydes. They have also been prepared by the electrolytic reduction of substituted benzoic acids.

		Ortho-	Meta-	Para-
Chloro-benzyl alcohol . .	m.p.	72°	liquid	73°
Bromo-benzyl alcohol . .	,,	80°	,,	72°
Bromo-benzyl bromide . .	,,	30°	41°	61°
Nitro-benzyl alcohol . .	,,	74°	27°	93°
Nitro-benzyl chloride . .	,,	47°	46°	71°

o-Nitro-benzyl alcohol results also from the electrolytic oxidation of o-nitro-toluol (C. 1901, II. 1051); and p-nitro-benzyl alcohol by oxidation of p-nitro-toluol with MnO_2 and concentrated SO_4H_2 (German patent 212,949). The o-nitro-benzyl alcohol is reduced by zinc dust and sal-ammoniac solution to **o-hydroxylamino-benzyl alcohol** $HONH[2]C_6H_4CH_2OH$, m.p. 104°, which is oxidised by chromic acid to **azoxy-benzyl alcohol** $ON_2(C_6H_4CH_2OH)_2$, m.p. 123°; and by Caro's acid or ferric chloride to **o-nitroso-benzyl alcohol** $ON[2]C_6H_4CH_2OH$, m.p. 101°. The latter, on being boiled in water, loses H_2O and passes into *anthranile* (B. **36,** 836), and forms the link in the transition of o-nitro-toluol into anthranilic acid on heating with alkaline hydroxide.

Reduction of the nitro-benzyl alcohols, as well as the electrolytic reduction of nitro- and amido-benzoic acids in acid solution, produce amido-benzyl alcohols. **p-Amido-benzyl alcohol,** m.p. 64° (A. **305,** 119), is converted by acids into an *anhydro*-form $\left(C_6H_4\begin{matrix}CH_2\\|\\NH\end{matrix}\right)_2$, which is also obtained, with other derivatives, by direct action of formaldehyde upon the corresponding anilines in the presence of acids (B. **31,** 2037; **33,** 250; **35,** 739; C. 1898, II. 159; *Ch. Ztg.* **24,** 284).

p-Amido-benzyl-amine $NH_2C_6H_4CH_2NH_2$ b.p. 269°; **p-Acetyl-amido-N-chloracetyl-benzyl-amine** $CH_3CONHC_6H_4CH_2NHCOCH_2Cl$ is produced by nuclear synthesis in the condensation of acetanilide with **methyiol-chloracetamide** $CH_2ClCONH.CH_2OH$ under the action of concentrated H_2SO_4. On boiling with HCl the acetyl and chlor-acetyl groups are split off (A. **343,** 299).

p-Amido-benzyl-aniline $NH_2C_6H_4CH_2NHC_6H_5$ a viscous oil, from anhydro-formaldehyde-aniline with aniline; easily transposed to di-amido-diphenyl-methane (B. **29,** R. 746; C. 1900, I. 1112). **p-Nitro-benzyl-amine,** see B. **30,** 61.

m-Amido-benzyl alcohol $NH_2[3]C_6H_4[1]CH_2OH$, m.p. 92°, from m-nitro-benzoic acid by electrolytic reduction (B. **38,** 1751).

o-Amido-benzyl alcohol $NH_2[2]C_6H_4CH_2OH$, m.p. 82°, b.p.$_{10}$ 160°, is formed from o-nitro-benzyl alcohol or from anthranile by reduction with zinc dust and HCl (B. **25,** 2968; **27,** 3513); from anthranilic ester with Na amalgam in acid solution (B. **38,** 2062); and by electrolytic reduction of o-nitro-benzoic acid or anthranilic acid (B. **38,** 1751).

O-Acetyl-o-amido-benzyl alcohol $NH_2C_6H_4CH_2OCOCH_3$, an oil smelling of aniline, with a chlorohydrate melting at 116°, is formed by the reduction of o-nitro-benzyl acetate. The free base is unstable, and on standing, or (rapidly) on heating, it passes into the crystalline N-acetate $CH_3CONHC_6H_4CH_2OH$, m.p. 116°. Cold HBr converts the latter into the bromohydrate of μ-methyl-pheno-pentoxazol, which, on standing in water, takes up water and splits up to form O-acetyl-o-amido-benzyl alcohol (B. **37,** 2249).

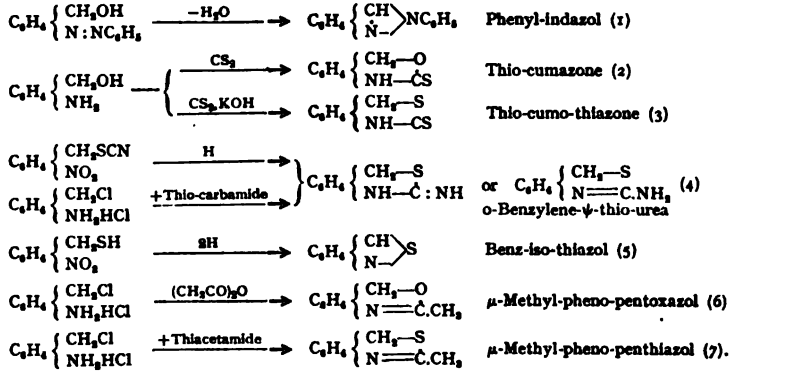
Formation of Hetero-rings from Derivatives of o-Amido-benzyl Alcohol.—Just like the o-diamines, o-amido-phenols, and o-amido-thio-phenols, many o-amido-benzyl alcohol derivatives, and also those of o-nitro-benzyl alcohol, so far as they yield o-amido-benzyl alcohol compounds upon reduction, show ability to form hetero-rings. Some

of the derivatives of these two alcohols capable of yielding hetero-rings are the following :

· o-Amido-benzyl alcohol combines with nitroso-benzol to **o-benzol-azo-benzyl alcohol** $C_6H_5N : NC_6H_4CH_2OH$, m.p. 78°, which, on heating with H_2SO_4, becomes *phenyl-indazol* (C. 1903, I. 1416). It becomes *thio-cumazone* (B. **27,** 1866) when it is boiled with alcoholic CS_2, and *thio-cumo-thiazone* (B. **27,** 2427) when the CS_2 and alcoholic potash are used. The urea derivatives of o-amido-benzyl alcohol lead to similar rings (B. **27,** 2413).

o-Nitro-benzyl sulpho-cyanide $NO_2C_6H_4CH_2S.CN$, m.p. 75° (B. **25,** 3028), yields o-benzylene-ψ-thio-urea. Sulphuric acid reduces it to o-nitro-benzyl-carbamine-thiolic ester $NO_2.C_6H_4CH_2.SCONH_2$, m.p. 116°. Hydrochloric acid saponifies this to **o-nitro-benzyl mercaptan** $NO_2[2]C_6H_4[1]CH_2SH$, m.p. 43°. Both bodies yield benz-iso-thiazol upon reduction (B. **28,** 1027 ; **29,** 160).

o-Amido-benzyl chloride hydrochloride $HCl.NH_2.C_6H_4CH_2Cl$ is formed by the action of concentrated hydrochloric acid upon o-amido-benzyl alcohol. With caustic potash this yields **poly-o-benzylene-imide** $(C_7H_7N)_x$(B. **19,** 1611 ; **28,** 918, 1651) ; with acetic anhydride, *μ-methyl-pheno-pentoxazol* ; with thiacetamide, *μ-methyl-pheno-penthiazol* (B. **27,** 3515) ; and with thio-urea, *o-benzylene-ψ-thio-urea* (B. **28,** 1039) :



The anhydride of an o-benzyl-alcohol-sulphonic acid, **sulpho-benzide** $C_6H_4\begin{cases}[1]SO_2\\[2]CH_2\end{cases}O$, m.p. 113°, is obtained by the reduction of the stable o-sulpho-benzoic acid chloride, much as the phthalide is obtained from phthalyl chloride ; also by reduction of the product of the action of PCl_5 upon o-benzaldehyde-sulphonic acid (B. **31,** 1666).

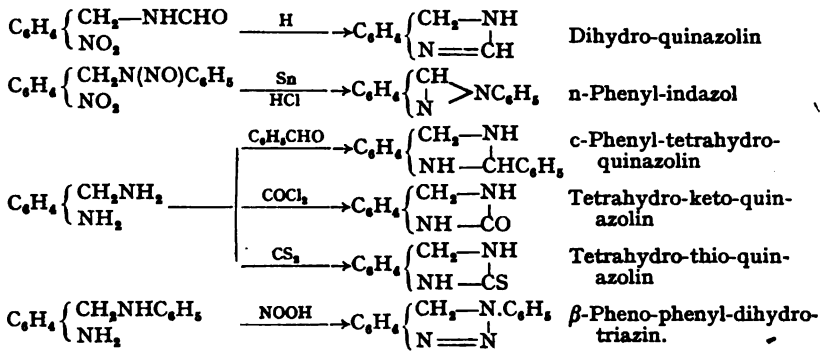
o-Nitro-benzyl-amine $C_6H_4(NO_2).CH_2.NH_2$, obtained from o-nitro-benzyl chloride by the saponification of its phthalimide derivative, is a strong, oily base (B. **20,** 2227).

o-Nitro-benzyl-formamide $NO_2.C_6H_4.CH_2.NH.CHO$, melting at 89°, is reduced to *dihydro-quinazolin* (B. **25,** 3031 ; **36,** 806).

o-Nitro-benzyl-aniline $NO_2.C_6H_4.CH_2.NHC_6H_5$, melts at 44° (B. **19,** 1607).

o-Nitro-benzyl-phenyl-nitrosamine $NO_2C_6H_4CH_2N(NO)C_6H_5$ is converted by tin and hydrochloric acid into *n-phenyl-indazol* (B. **27,** 2899).

o-Amido-benzyl-amine, *o-benzylene-diamine* $NH_2C_6H_4CH_2NH_2$ is a radiating crystalline mass, obtained from o-nitro-benzyl-amine. With aldehydes like benzaldehyde it forms *phenyl-tetrahydro-keto-quinazolin*; with phosgene, *tetrahydro-keto-quinazolin*; with carbon disulphide, *tetrahydro-thio-quinazolin* (B. **28,** R. 238). **o-Amido-benzyl-aniline** $NH_2.C_6H_4.CH_2.NH.C_6H_5$, melting at 86°, forms *β-pheno-phenyl-dihydro-triazin* with nitrous acid (B. **25,** 448).



(2) Aromatic Monaldehydes.

The aromatic monaldehydes are the first oxidation products, and correspond to the primary aromatic monohydric alcohols. They are very similar to the fatty aldehydes so far as their rearrangements, dependent upon the reactivity of the aldehyde group, are concerned.

Formation.—(1) By the oxidation of the primary monohydric, aromatic alcohols. (2) By the distillation of the calcium salts of the aromatic monocarboxylic acids with calcium formate. (3) From their halogen derivatives $C_6H_5.CHCl_2$, with water, especially in the presence of sodium carbonate, lime, or lead oxide, or by heating with anhydrous oxalic acid. (4) Technically, by oxidising benzyl chloride with lead nitrate. (5) A very interesting and direct conversion of homologous benzenes into aldehydes is that occurring in the action of chromyl chloride CrO_2Cl_2. The first products are pulverulent, brown addition compounds $C_6H_5CH_3(CrO_2Cl_2)_2$, which decompose into aldehydes when they are introduced into water (B. **17,** 1462; **21,** R. 714; **32,** 1050). On oxidising methyl-benzols with chromic acid in the presence of acetic anhydride at 0°, diacetates of ortho-aldehydes are formed, *e.g.* $NO_2C_6H_4CH(OCOCH_3)_2$, $C_6H_4[CH(OCOCH_3)_2]_2$. Manganese peroxide, cerium oxide with sulphuric acid, or manganese persulphate also oxidise alkyl-benzols in the cold to aromatic aldehydes (C. 1901, II. 70, 1154; 1906, II. 1297, 1589). By electrolytic oxidation also, aldehydes can be obtained from alkyl-benzols (C. 1905, II. 763). (6) During oxidation of olefin-benzols with ozone, they are split at the ethylene link, with formation of aldehydes (B. **37,** 842, 2304; **41,** 2751; A. **343,** 311):

$$C_6H_5CH_2CH : CHCH_3 \longrightarrow C_6H_5CH_2CHO.$$

(7) From the aromatic primary-secondary and primary-tertiary

ethylene glycols, and from the corresponding ethylene oxides, by heating with dilute H_2SO_4 or alone (C. 1905, II. 1628; B. **39**, 2288):

$$C_6H_5(CH_3)COHCH_2OH \longrightarrow C_6H_5(CH_3)CH.CHO \longleftarrow C_6H_5(CH_3)\overset{O}{\diagup\diagdown}CH{-}CH_2.$$

The secondary-tertiary phenyl-ethylene glycols, in which phenyl is held by a secondary link, yield aldehydes on displacement of the phenyl group:

$$C_6H_5CH(OH)C(OH)(CH_3)_2 \longrightarrow OCH.C\begin{cases}(CH_3)_2\\C_6H_5\end{cases}.$$

The formation of aldehydes from the iodo-hydrins of some olefin-benzols by treatment with NO_3Ag or HgO (C. 1907, I. 1577; 1909, I. 1335):

$$C_6H_5CH(OH).CHI.CH_3 \longrightarrow OCH.CH\begin{cases}C_6H_5\\CH_3\end{cases}$$

also leads to the formation of aldehydes.

(8) From phenyl-nitro-methanes by reduction, and from β-benzyl-hydroxylamines by oxidation, oximes of the aromatic aldehydes are obtained, and from these the aldehydes may be obtained by hydrolysis (C. 1899, I. 1073).

(9*a*) *Synthetically*, the aldehydes are obtained from the aromatic hydrocarbons by the action of carbon monoxide and HCl in the presence of Cu_2Cl_2 and Al chloride or bromide (A. **847**, 347):

$$C_6H_6+CO+HCl \xrightarrow[Cu_2Cl_2]{Al_2Cl_6} C_6H_5CHO.$$

(9*b*) *Benzaldoximes* $C_6H_5CH:NOH$ are similarly produced from benzene, detonating mercury $C:NHgO$, and Al chloride containing water of crystallisation. Dry Al chloride forms chiefly nitriles (B. **36**, 322).

(10) Aromatic aldehydes are also formed by the action of aryl-magnesium haloids on excess of formic ester (B. **36**, 4152; C. 1905, I. 309; cp. also *Ch. Ztg.* **29**, 667):

$$C_6H_5CH_2MgCl+HCOOC_2H_5 \longrightarrow C_6H_5CH_2CHO+ClMgOC_2H_5.$$

By using ortho-formic ester the corresponding acetals are obtained (C. 1904, I. 509, 1077; B. **37**, 186).

The formic ester can often be advantageously replaced by **ethoxy-methylene-aniline** $C_6H_5N:CHOC_2H_5$. From the benzylidene-anilines first formed the aldehydes are easily obtained by boiling with dilute acids (C. 1906, I. 1487).

(11) The condensation products $ArCHOH.CCl_3$, obtained from aryl-magnesium haloids and chloral on boiling with potassium carbonate solution, split up into chloroform and aldehydes (C. 1908, I. 1388):

$$C_6H_5MgBr \xrightarrow{CCl_3CHO} C_6H_5CH(OH)CCl_3 \longrightarrow C_6H_5CHO+CHCl_3.$$

(12) The aryl-glycidic acids obtained from aromatic ketones by condensation with chloracetic ester, and Na ethylate or amide, easily break up into CO_2 and aldehydes (C. 1905, I. 346; B. **38**, 699):

$$C_6H_5COCH_3 \xrightarrow{CH_2ClCO_2R} C_6H_5(CH_3)\overset{O}{\diagup\diagdown}C{-}CH.CO_2H \xrightarrow{-CO_2} C_6H_5(CH_3)CH.CHO.$$

(13) Benzoyl-formic acid $C_6H_5.CO.COOH$ and its homologues, easily formed by synthesis, are converted, by heating with aniline, into benzylidene-anilines, which may be readily split up into aldehydes and aniline (C. 1903, I. 832, etc.).

(14) The acidyl-phenyl-glycolic esters (*q.v.*) and phenyl-tartronic esters (*q.v.*), obtained by the condensation of **αβ-diketone-carboxylic esters** or **mesoxalic esters** with benzols, tertiary anilines, or phenols, may be converted into the corresponding aldehydes, (I.) by warming with concentrated H_2SO_4, or (II.) by oxidation with copper acetate and decomposition of the resulting benzoyl-formic acids (C. 1910, I. 25) :

I. $C_6H_5C(OH)(COCH_3)CO_2CH_3+H_2O = C_6H_5CHO+CH_3COOH+CH_3OH+CO.$
II. $C_6H_5C(OH)(COCH_3)CO_2CH_3+O+H_2O = C_6H_5CO.COOH+CH_3COOH+CH_3OH.$

Properties.—Benzaldehyde and its homologues are mostly liquid bodies, which possess an aromatic odour, and reduce ammoniacal silver solutions with the production of a metallic mirror. (1) They are readily oxidised to carboxylic acid. (2) They differ from the fatty aldehydes in that they are, as a general rule, readily oxidised to alcohols and acids by alcoholic or aqueous alkalies; it appears that this reaction is, however, only peculiar to those aldehydes in which the CHO group is in direct union with the benzene nucleus. (3) Nascent hydrogen reduces them to alcohols when they are in part, through the union of two aldehyde residues, converted into *hydro-benzoïns*. (4) They combine with acid alkaline sulphites. (5) With hydroxylamine they yield *aldoximes*, which manifest rather remarkable isomeric relations. (6) They form *phenyl-hydrazones* with phenyl-hydrazin. (7) With primary amines : aldehyde imines (Schiff's bases). (8) With the salts of nitro-hydroxylaminic acid NaON : NOONa and benzol-sulphydroxamic acid they form *hydroxamic acids* (C. 1904, I. 1204). (9) Phosphorus pentachloride replaces their aldehyde oxygen by two atoms of chlorine. (10) Chlorine substitutes aldehyde hydrogen.

They do not polymerise, as do the first members of the group of fatty aldehydes.

Nuclear Syntheses.—(1) In the reduction of aromatic aldehydes—*e.g.* in the electrolytic reduction (B. **29,** R. 229; C. 1907, I. 339)—there occurs, along with alcohol formation, a production of *hydro-benzoïn* analogous to the pinacone formation :

$$2C_6H_5CHO+2H = C_6H_5CH(OH)—CH(OH).C_6H_5 \text{ hydro-benzoïn.}$$

(2) A very interesting reaction of the aldehydes is their conversion into benzoïns, through the agency of alcoholic potassium cyanide. Two aldehyde molecules combine to a polymeric body :

$$2C_6H_5CHO = C_6H_5CH(OH).CO.C_6H_5 \text{ benzoïn.}$$

See B. **29,** 1729; **31,** 2699, for the condensations of benzylidene-aniline and benzaldehyde by potassium cyanide.

(3) The aromatic aldehydes combine with the most heterogeneous bodies—*e.g.* aldehydes, ketones, monocarboxylic acids, dicarboxylic acids, etc.—water always disappearing.

These so-called *condensation reactions* proceed similarly to the *aldol*-condensation, only there is generally an elimination of water, as in the

conversion of aldol into *croton-aldehyde*. The condensation agents are HCl gas, zinc chloride, sulphuric acid, glacial acetic acid, acetic anhydride, dilute sodium hydroxide, baryta water, a solution of potassium acetate, and potassium cyanide (primary, secondary, and tertiary bases).

In this manner benzaldehyde can undergo the following rearrangements without difficulty :

C_6H_5CHO —CH_3COOH→	$C_6H_5CH=CH.COOH$	Cinnamic acid
—CH_3CHO→	$C_6H_5CH=CH.CHO$	Cinnamic aldehyde
—CH_3COCH_3→	$C_6H_5CH=CH.CO.CH_3$	Benzal-acetone
—$CH_2(COOH)_2$→	$C_6H_5CH=C(COOH)_2$	Benzal-malonic acid
—$CH_3COCH_2CO_2C_2H_5$→	$C_6H_5CH=C<^{CO_2C_2H_5}_{COCH_3}$	Benzal-aceto-acetic ester.

Pyrones $CO[C(CH_3):C(C_6H_5)]_2O$ (B. **29**, 1352) result when two molecules of benzaldehyde condense with ketones like diethyl-ketone. *Pyridin* derivatives result when benzaldehyde and aceto-acetic ester condense with ammonia and aniline ; whereas benzylidene-diaceto-acetic esters are formed under the influence of aliphatic amines (B. **29**, R. 841).

The benzaldehydes also condense with phenols and anilines, forming derivatives of triphenyl-methane.

Benzaldehyde, *bitter-almond oil, benzyl hydride* $C_6H_5.CHO$, b.p. 179°, with specific gravity 1·050 (15°), is a colourless liquid with high refractive power. Formerly it was prepared exclusively from its glucoside amygdalin (see below). At present it is only the officinal bitter-almond oil water, *aqua amygdalarum amararum*, in which hydrocyanic acid is the active ingredient, that is made from the amygdalin. It has the characteristic agreeable " bitter-almond oil " odour. It is soluble in thirty parts water, and is miscible with alcohol and ether. Benzaldehyde does not occur already formed in the bitter almonds, but is produced, as demonstrated by Wöhler and Liebig in 1831, from the glucoside *amygdalin* contained in the oil. This is easily converted, by boiling with dilute acids or upon standing in contact with the unorganised ferment *emulsin*, also present in bitter almonds, into benzaldehyde, glucose, and hydrocyanic acid.

Amygdalin : $C_{20}H_{27}NO_{11}+2H_2O=C_6H_5CHO+2C_6H_{12}O_6+CNH$.

In the general methods common to the formation of all aldehydes, reactions were indicated which would lead to the production of benzaldehyde. Thus it is formed (1) from benzyl alcohol ; (2) from calcium benzoate and formate ; (3) from benzal chloride ; (4) from benzyl chloride, from which it is prepared technically by oxidation with lead nitrate ; (5) from toluol and chromyl chloride CrO_2Cl_2 ; (6) from benzene and CO with HCl, Cu_2Cl_2, and Al_2Br_6 ; and (7) from phenyl-magnesium bromide and formic ester or its derivatives.

In describing the transformations of the aldehydes, benzaldehyde was chosen as the example. It even absorbs oxygen from the air and becomes benzoic acid, and when mixed with acetic anhydride and sand it not only yields benzoic acid but also *benzoyl-hydrogen peroxide*

$(C_6H_5COO)_2$ (B. **27**, 1959). Sodium amalgam reduces it to benzyl alcohol and hydro-benzoïn, while PCl_5 changes it to benzal chloride. It shows both oxime and phenyl-hydrazone formation, etc.

With sulphurous acid it combines to an oxy-sulphonic acid soluble in water, from which the aldehyde can be recovered by simple heating. This process can be utilised for regenerating benzaldehyde (C. 1904, I. 1145).

Homologous Benzaldehydes.—*o-*, *m-*, and *p-Toluic aldehydes* boil at 200°, 199°, and 204°. The o- and m-bodies smell like benzaldehyde, while the p-compound has an odour like that of pepper.

α-Toluic aldehyde, phenyl-acetaldehyde $C_6H.C_5H_3.CHO$, boiling at 206°, and isomeric with the three toluic aldehydes, is produced (1) by distillation of α-toluate of calcium and calcium formate; (2) when chromyl chloride and water act upon ethyl-benzene; (3) by acting with water on β-bromo-styrolene; (4) by heating phenyl-lactic acid or phenyl-glycidic acid with dilute sulphuric acid; (5) from **phenyl-α-chloro-lactic acid** $C_6H_5.CH(OH).CHCl.CO_2H$, by the action of alkalies (B. **16**, 1286; A. **219**, 179); and (6) from **phenyl-glyceric acid** or its β-lactone $C_6H_5CH(O)CH(OH)CO$, by heating alone or in water (C. 1900, I. 887). Phenyl-acetaldehyde has a sweetish odour resembling that of hyacinths, and is used in perfumery. It polymerises easily on keeping. On heating with alcoholic potash it forms a mixture of triphenyl-benzol and 1, 3-diphenyl-tetramethylene (B. **38**, 1965). **α-Phenyl-propyl-aldehyde,** *hydro-atropa-aldehyde* $C_6H_5(CH_3)CH.CHO$, b.p. 204°, is obtained from unsym. phenyl-methyl-glycol by heating with dilute H_2SO_4 (B. **39**, 2297), from phenyl-methyl-glycidic acid or unsym. phenyl-methyl-ethylene oxide on heating alone (B. **38**, 704; C. 1905, II. 1628). **α-Phenyl-butyraldehyde** $(C_6H_5)CH.CHO$, b.p. 211°, from unsym. phenyl-ethyl-glycol (B. **39**, 2300). **α-Propyl-** and **α-iso-butyl-phenyl-acetaldehyde,** b.p.$_{28}$ 122°, b.p.$_{30}$ 153°, **α-Methyl-phenyl-propyl-aldehyde,** b.p.$_{19}$ 130°, from the corresponding glycidic acids by method 12 (C. 1905, I. 347).

Phenyl-propyl-aldehyde, *hydro-cinnamic aldehyde* $C_6H_5CH_2CH_2CHO$, b.p.$_{13}$ 105° (B. **31**, 1992), is best obtained by reduction of cinnamic aldehyde acetal. **3, 5-Dimethyl-benzaldehyde, mesityl-aldehyde** $(CH_3)_2C_6H_3CHO$, b.p. 221°, from mesitylene bromide (*J. pr. Ch.* 2, **58**, 359). **2, 5-Dimethyl-benzaldehyde,** b.p.$_{10}$ 100°, is obtained from p-xylol-glyoxylic acid by method 13; while from p-xylol, CO, and HCl, etc., by method 9, 2, 4-dimethyl-benzaldehyde is formed, with migration of atoms (C. 1903, I. 830).

Cumic aldehyde, cuminol, *p-iso-propyl-benzaldehyde* $(CH_3)_2CH[4]C_6H_4[1]CHO$, boiling at 235°, with specific gravity 0·973 (13°), occurs, together with cymene, in Roman carraway oil, and in oil of *Cicuta virosa*, or water-hemlock (B. **26**, R. 684). Cuminol possesses an aromatic odour. Dilute nitric acid oxidises it to cumic acid; chromic acid converts it into terephthalic acid. *Cumic acid* (*q.v.*) and *cumyl alcohol* are produced when it is digested with alcoholic potash. When distilled with zinc dust, cymol results.

Derivatives of Benzaldehyde.

Haloid Derivatives.—The halogen compounds corresponding to benzaldehyde are obtained by the action of PCl_5 or PBr_5 upon it.

Benzal chloride, benzylidene chloride, chloro-benzene, chloride of bitter-almond oil, $C_6H_5CHCl_2$, boiling at 213°, with specific gravity 1·295 (16°), results from the action of chlorine upon boiling toluene, from toluene (A. **189**, 318; **146**, 322) and PCl_5 at 170°–200°, as well as from benzaldehyde and $COCl_2$ (*Z. f. Ch.* 2, **7**, 79). It changes to benzaldehyde when it is heated to 140°–160° with water, or to 60°–70° with anhydrous oxalic acid. *Benzal bromide* boils at 130°–140° (20 mm.). Acetals of the aromatic aldehydes are obtained from these with dilute alcoholic HCl, or with orthoformic ester, and from the aldehyde chlorides with sodium alcoholates (B. **31**, 1989; **40**, 3903).

Benzal dimethyl and *diethyl ether*, boiling at 208° and 220°, *benzal diacetyl ester*, melting at 44° and boiling at 220° (A. **102**, 368; **146**, 323), are produced when sodium methylate, sodium ethylate, and silver acetate act upon benzal chloride. The diethyl ether is also formed from benzaldehyde and orthoformic ester (B. **29**, 247), as well as from benzylidene-imide hydrochloride with alcohol.

Sulphur Derivatives of Benzaldehyde.—Compare the thio-acetaldehydes: *α-* and *β-trithio-benzaldehyde* melt at 167° and 225° (B. **29**, 159). Polymeric *thio-benzaldehyde* melts at 83° (B. **24**, 1428). When heated with finely divided copper they yield *stilbene* $C_6H_5.CH=CH.C_6H_5$.

On mercaptals and sulphones from benzaldehydes, see B. **35**, 2343.

Benzaldehyde-potassium bisulphite, *potassium-oxy-benzyl sulphonate* $C_6H_5CH(OH)SO_3K+\frac{1}{2}H_2O$, see A. **85**, 186.

Sodium-benzaldehyde sulphoxylate $C_6H_5CH(OH)O.SONa$; on addition of benzaldehyde to a feebly alkaline sodium hydrosulphite solution, it is precipitated in flakes. The secondary salt is more stable than the primary (B. **42**, 4634).

Nitrogenated Benzaldehyde Derivatives.—Phenyl-dinitro-methane $C_6H_5CH(NO_2)_2$, m.p. 79°, is formed by the action of N_2O_4 upon benzaldoxime or **acetyl-benzoyl oxime** $C_6H_5C(NOH).COCH_3$; on heating to 130° it forms benzaldehyde, and by reduction with Al amalgam benzylamine and NH_3 (*J. pr. Ch.* 2, **65**, 197; **73**, 494; C. 1901, II. 1007; 1906, II. 1003). On the action of diazo-benzol chloride upon phenyl-dinitro-methane, see C. 1909, II. 905.

When ammonia acts at −20° upon a concentrated alcoholic solution of benzaldehyde, the first product is the very unstable benzaldehyde ammonia $(C_6H_5CHOH)_2NH$, m.p. 45°, which quickly breaks up into benzaldehyde, water, and **hydrobenzamide**, *tribenzal-diamine* $(C_6H_5CH)_3N_2$, melting at 110°. When this body is heated it is transposed to *amarine* or *triphenyl-dihydro-glyoxaline* (*q.v.*). When hydrochloric acid gas is conducted into the alcoholic benzene solution of hydro-benzamide, *benzylidene imide* $C_6H_5CH:NH.HCl$, melting with decomposition at 180°, separates. Water immediately resolves this body into benzaldehyde and ammonium chloride (B. **29**, 2144; **42**, 2216).

Benzal-ethyl-amine $C_6H_5.CH:N.C_2H_5$, b.p. 195°. **Benzal-aniline**, *benzylidene-aniline* $C_6H_5.CH:N.C_6H_5$, m.p. 45°, from benzaldehyde and aniline, with elimination of water. In the presence of concentrated HCl the aromatic aldehydes combine with anilines to chlorohydrates of the aldehyde-anilines, like $C_6H_5CH(OH)NHC_6H_5.HCl$, which sometimes, especially in the oxy-benzaldehydes, represent fairly stable compounds; the free hydrates, on the other hand, usually lose H_2O readily, and pass into the benzylidene compounds (Schiff's bases.

B. **85,** 984). In a few cases Schiff's bases, like the benzaldoximes, occur in two isomeric forms (B. **43,** 3359). On the nitrogenation and sulphuration of benzylidene-anilines, see C. 1903, I. 231. With benzaldehyde in alcoholic KCN solution benzaniline does not give the benzoïn reaction, but a complex condensation takes place with the help of hydrocyanic acid (see B. **38,** 1761). On the condensation of benzaniline with malonic ester, aceto-acetic ester, and similar bodies, see B. **31,** 2596; **32,** 332; **36,** 937.

Benzylidene-p-amido-dimethyl-aniline $C_6H_5CH : NC_6H_4N(CH_3)_2$, m.p. 99°, yellow needles, forms, with one molecule HCl a red, and with two molecules HCl a white, chlorohydrate (C. 1908, I. 1539).

When the o-phenylene-diamines and benzaldehyde interact, the bodies resulting at first are: **benzylidene-o-phenylene-diamine** $NH_2.C_6H_4N : CH.C_6H_5$, m.p. 61°, and **dibenzylidene-o-phenylene-diamine** $C_6H_4[N : CH.C_6H_5]_2$. However, they readily rearrange themselves into isomeric, ring-shaped imidazole derivatives, or aldehydes (B. **29,** 1497). The amidated benzylidene-anilines and **bis-benzylidene-p-phenylene-diamines,** like $NH_2C_6H_4.CH : N.C_6H_4N : CHC_6H_4NH_2$ have dyeing properties similar to those of the amido-azo-bodies; the azomethine group —CH : N— is a "chromophore," like the azo-group —N=N—, but to a much smaller extent (B. **31,** 2250). In both cases the introduction of "auxo-chromic" groups (NH_2, OH, etc.) produces a deepening of the colour (C. 1907, I. 106).

Benzylidene-hydrazin, *benzal-hydrazin* $C_6H_5CH : NNH_2$, m.p. 16°, b.p.$_{14}$ 140°, is formed from hydrazin hydrate with benzaldehyde and barium oxide, and from benzalazin by boiling with hydrazin hydrate. It easily passes into benzalazin in various ways; with acetic anhydride it gives benzal-acetyl-hydrazin $C_6H_5CH : N.NHCOCH_3$, m.p. 134°, which is also formed from acetyl-hydrazin and benzaldehyde (B. **85,** 3234).

Benzalazin $C_6H_5CH : N.N : CHC_6H_5$, m.p. 93°, from benzaldehyde and hydrazin, decomposed by heat into nitrogen and *stilbene.* By reduction with zinc dust and glacial acetic acid it splits off NH_3 and yields dibenzyl-amine. By sodium amalgam it is first converted into benzyl-benzylidene-hydrazin and further into sym. dibenzyl-hydrazin. With bromine it unites to form a tetrabromide, which readily decomposes with evolution of nitrogen (cp. *J. pr. Ch.* 2, **58,** 372). With dimethyl sulphate the benzalazin combines to form an ammonium compound $C_6H_5CH : N(CH_3)(OSO_3CH_3)N : CHC_6H_5$ which, with water, breaks up into benzaldehyde and methyl-hydrazin (A. **376,** 244). On the influence of magnesium organic compounds upon benzalazin, see B. **43,** 740.

Benzal-phenyl-hydrazone $C_6H_5CH : NNHC_6H_5$, m.p. 152° (A. **190,** 134), is converted by acetic anhydride and H_2SO_4 into a stereo-isomeric body of m.p. 136°; sodium amalgam reduces it to sym. benzyl-phenyl-hydrazin. On oxidation, the benzal-phenyl-hydrazones yield *dibenzal-diphenyl-hydro-tetrazone, benzile-osazone, dehydro-benzal-phenyl-hydrazone* and *tetraphenyl-tetrazolin* $\begin{matrix} C_6H_5C=N-NC_6H_5 \\ C_6H_5N-N=CC_6H_5 \end{matrix}$ (B. **34,** 523).

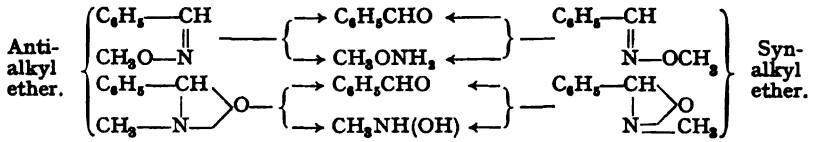
Numerous benzal compounds of hydrazin derivatives have been prepared; they serve to characterise the latter.

Benzaldoximes.—The interaction of hydroxylamine and benzalde-

hyde produces **α-benzaldoxime,** *benzantialdoxime,* m.p. 35° and b.p. 117° (14 mm.). Hydrochloric acid, sulphuric acid, or bromine changes it, with the simultaneous production of unstable salts (B. **27,** R. 599), into **β-benzaldoxime, iso-benzaldoxime, benzo-synaldoxime,** m.p. 125°. For another method, see A. **365,** 202. When this body is distilled under reduced pressure, it passes into the α-derivative. Each of these isomerides gives rise to two structurally isomeric series of *alkyl ethers,* in one of which the alkyl is joined to oxygen, in the other to nitrogen, as the first, upon decomposition, yield α-, and the second β-alkyl-hydroxylamines. Hantzsch and Werner attribute the isomerism of the α- and β-aldoximes to the spatial arrangement of the hydroxyl group with reference to nitrogen. The oximes are distinguished as benzanti- and benzo-synaldoxime (B. **24,** 3481). The sym. configuration would fall to the β-aldoxime, because in a series of reactions—*e.g.* treatment of the acid ester with alkalies—it changes more readily and completely to *benzo-nitrile* than the α-body :

(α-) Benzantialdoxime $\overset{C_6H_5CH}{HO\dot{N}}$ (β-) Benzo-synaldoxime $\overset{C_6H_5CH}{\dot{N}OH}$.

The following formulæ would then correspond to the N- and O-alkyl ethers of these compounds :



The benzaldoximes and phenyl cyanate combine to isomeric phenyl-urethane derivatives $C_6H_5CH : NOCONHC_6H_5$. The N-alkyl ethers also unite with phenyl cyanate, forming azoxazol (furo-*ab'*-diazol) derivatives (B. **27,** 1957) :

$$\begin{matrix} C_6H_5CH \\ C_7H_7\dot{N} \end{matrix}\!\!>\!O \xrightarrow{C_6H_5NCO} \begin{matrix} C_6H_5CH.N(C_6H_5) \\ C_7H_7\dot{N}\text{———}O \end{matrix}\!\!>\!CO.$$

Benzaldoxime is also produced from benzyl-amine by oxidation with Caro's acid, and is further oxidised by that agent to phenyl-nitromethane and benzo-hydroxamic acid (B. **34,** 2023, 2262).

Anti-benzaldoxime-o-methyl ether is an oil, b.p. 191°. It results from the interaction of α-benzaldoxime with sodium alcoholate and methyl iodide or with diazo-methane (C. 1909, I. 1754). Hydrochloric acid resolves it into benzaldehyde and α-methyl-hydroxylamine. **N-Methyl ether** melts at 45°–49°. Its hydrobromide is formed on heating α-benzaldoxime, methyl, bromide, and methyl alcohol in a sealed tube to 85°. On exposure it rearranges itself into the syn-form (B. **29,** R. 866 ; A. **365,** 215). **Syn-benzaldoxime-N-methyl ether,** melting at 82°, is formed, together with the isomeric o-ether, from syn-benzaldoxime, methyl iodide, and sodium ethylate (B. **24,** 2812), or by the action of the chloride of β-methyl-hydroxylamine upon benzaldehyde (A. **365,** 205). By the action of PCl_5 in etheric solution it is transposed into the **isomeric monomethyl-benzamide :**

$$C_6H_5\overline{CH.O.NCH_3} \longrightarrow C_6H_5CO.NHCH_3.$$

Benzaldoxime-O-benzyl ether $C_6H_5CH : NOCH_2C_6H_5$ is also known in a liquid and a solid modification, m.p. 31°. **p-Chloro-benzaldoxime-p-chloro-benzyl ether,** m.p. 114°, and **p-bromo-benzaldoxime-p-bromo-benzyl ether,** m.p. 130°, see B. **33,** 1975. These substances can only be split up with difficulty into aldehydes and hydroxylamines.

Benzaldoxime-N-benzyl ether $C_6H_5\overline{CH.O.N}CH_2C_6H_5$, m.p. 82°, is obtained from sodium iso-benzaldoxime with benzyl chloride, and from β-dibenzyl-hydroxylamine by oxidation. Benzaldoxime-N-benzyl ethers with nuclear substitution are transposed in a peculiar manner by sodium ethylate (A. **298,** 187) :

$$XC_6H_4\overline{CH.O.N}CH_2C_6H_5 \longrightarrow XC_6H_4CH_2\overline{N.O.C}HC_6H_5.$$

N-Phenyl-benzaldoxime $C_6H_5CH\langle^{O}_{NC_6H_5}$, melting at 109°, results from the union of benzaldehyde with β-phenyl-hydroxylamine (p. 78) (B. **27,** 1958 ; C. 1898, II. 80).

Benzantialdoxime acetate $C_6H_5CHNO(OC.CH_3)$ melts at 15° (B. **27,** R. 599).

Benzaldoxime peroxide $C_6H_5CH : N.O.ON : CHC_6H_5$, m.p. 105° with decomposition, results from the oxidation of benzaldoxime with sodium hypochlorite, or amyl nitrite, and also, together with benzo-nitrolic acid, from the action of nitrous acid upon phenyl-iso-nitro-methane. On heating with chloroform it undergoes a peculiar transformation into *dibenzenyl-azoxime* $C_6H_5C\langle^{N—C.C_6H_5}_{O\ \ N}$ (B. **39,** 2522).

Benzaldoxime-N-carbonamide $C_6H_5CH.O.N.CONH_2$, m.p. 125°, from benzaldehyde and hydroxyl-urea (Vol. I.). On heating it breaks up into α-benzaldoxime, benzo-nitrile, and cyanic acid (C. 1908, I. 948).

Benzaldoxime-O-acetic acid $C_6H_5CHN(OCH_2COOH)$ melts at 98°, the *N-derivative* $C_6H_5CH\langle^{N.CH_2.COOH}_{O}$ at 183° with decomposition. They are formed when chloracetic acid acts upon potassium benzaldoxime. When decomposed, the first yields glycollic acid and the second amidoxyl-acetic acid $HO.NH.CH_2.COOH$ (I. 350) (B. **29,** R. 169). Isomerisms similar to those of the benzaldoximes are shown by many substituted benzaldoximes, ketoximes, the benzile-dioximes, etc.

Benzal-amido-sulphonic acid $C_6H_5.CH : NSO_3H$ results from benzaldehyde and amido-sulphonic acid (B. **25,** 472).

Substituted benzaldehydes behave towards oxidising and condensing agents like benzaldehyde itself. The formation of heterocyclic bodies from o-nitro- and o-amido-benzaldehyde is especially worthy of notice.

Haloid benzaldehydes are formed when oxalic acid or sulphuric acid (A. **272,** 148) acts upon the halogen benzal chlorides ; or by oxidising cinnamic acids containing halogens in the nucleus :

o-Chloro-benzaldehyde	melts at	−4° ;	boils at	213° ;	the **oxime**	melts at	75°
m-Chloro-benzaldehyde	,,	17° ;	,,	213° ;	,,	,,	70°
p-Chloro-benzaldehyde	,,	47° ;	,,	213° ;	,,	,,	106°
o-Bromo-benzaldehyde	,,	21° ;	**o-Iodo-benzaldehyde**		,,		37°
p-Bromo-benzaldehyde	,,	57° ;	**p-Iodo-benzaldehyde**		,,		73°.

See B. **29,** 875, for the *di-* and *tetrachloro-benzaldehydes.*

o-, m-, p-Iodoso-benzaldehydes $C_6H_4(IO)CHO$, and **o- m-, p-iodo-benzaldehydes** $C_6H_4(IO_2)(CHO)$, have been obtained from the corresponding iodide-chlorides (B. **29**, R. 774).

Nitro-benzaldehydes $NO_2C_6H_4CHO$. On dissolving benzaldehyde in nitro-sulphuric acid, the chief product is meta-nitro-benzaldehyde. o-Nitro-benzaldehyde is formed simultaneously (B. **14**, 2803). o-Nitro-benzaldehyde is obtained by the oxidation of o-nitro-benzyl alcohol (C. 1899, II. 950) or from o-nitro-cinnamic acid or its ester (B. **17**, 121). It results also from o-nitro-toluol by oxidation with manganese peroxide and sulphuric acid (C. 1907, I. 383) or manganese persulphate $(SO_4)_2Mn$ (C. 1906, II. 1590). Also, with its oxime, from the di-mercury compound of o-nitro-toluol by oxidation with HNO_2 (C. 1908, II. 209).

Para-nitro-benzaldehyde results (1) by the oxidation of p-nitro-cinnamic acid (B. **14**, 2577); (2) by allowing CrO_2Cl_2 and water to act upon p-nitro-toluol in carbon disulphide (B. **19**, 1061); (3) when p-nitro-benzyl chloride is boiled with water and lead nitrate, or when sulphuric acid acts upon p-nitro-benzal chloride.

The oximes of o- and p-nitro-benzaldehyde are obtained from o- and p-nitro-toluol by the action of amyl nitrite and sodium ethylate (C. 1899, II. 371; 1900, I. 886, 1273). In the form of their acetates $C_6H_4(NO_2)CH(OCOCH_3)_2$ they are obtained from o- and p-nitro-benzaldehyde by the oxidation of a solution of o- and p-nitro-toluol in acetic anhydride sulphuric acid with chromic acid (A. **311**, 355):

	M.p.		M.p.		M.p.
o-Nitro-benzaldehyde,	46°;	**oxime,**	103° (α), 149° (β);	**hydrazone,**	153°
m-Nitro-benzaldehyde,	58°;	,,	117° (α), 118° (β);	,,	121°
p-Nitro-benzaldehyde,	107°;	,,	130° (α), 174° (β);	,,	155°.

o- and p-Nitro-α- or anti-benzaldoximes pass, on illumination of their benzene solution, into the more stable β- or syn-aldoximes (B. **36**, 4268).

On the behaviour of the nitro-benzaldehydes in the animal organism, see B. **25**, 2457.

The effect of light on o-nitro-benzaldehyde in indifferent solvents is to transpose it entirely into **o-nitroso-benzoic acid** (*q.v.*). In alcoholic solution the corresponding **o-nitroso-benzoic esters** are produced, with the acetals of o-nitroso-benzaldehyde as intermediate products. The entry of a second substituent in o-position to the aldehyde group, connects the acetal formation and the power of transposition ("Steric Hindrance," A. **371**, 319). o-Nitro-benzaldehyde condenses with aldehyde and acetone, through the action of dilute caustic soda, to o-nitro-phenyl-lactic acid aldehyde and o-nitro-phenyl-lactic methyl ketone, which caustic soda converts into *indigo*:

$$C_6H_4\begin{cases}[1]CHO\\[2]NO_2\end{cases}\rightarrow\left\{\begin{array}{l}\xrightarrow{CH_3.CHO}C_6H_4\begin{cases}CH(OH).CH_2.CHO\\NO_2\end{cases}\\[2ex]\xrightarrow{(CH_3)_2CO}C_6H_4\begin{cases}CH(OH).CH_2.CO.CH_3\\NO_2\end{cases}\end{array}\right\}\rightarrow C_6H_4\begin{cases}CO\\NH\end{cases}>C:C<\begin{cases}CO\\NH\end{cases}C_6H_4.$$

Indigo.

5-Nitro-2-chloro-benzaldehyde $NO_2.C_6H_3Cl.CHO$, melts at 80°; its *oxime* at 147°. The latter is readily converted by boiling alkali into nitro-salicylic acid (B. **26**, 1253). **3-Nitro-4-bromo-benzaldehyde** $NO_2.C_6H_3BrCHO$ melts at 103°; its *oxime* at 145° (B. **24**, 3775). **2-Nitro-5-chloro-** and **-bromo-benzaldehyde,** m.p. 76° and 74° respectively, by

nitrogenation of m-chloro- and m-bromo-benzaldehyde respectively (B. **38,** 2811). **2-Nitro-4-chloro-** and **-bromo-benzaldehyde,** m.p. 67° and 98° respectively, are formed by a peculiar reaction from 4-amido-2-nitro-benzaldoxime on treatment with ferric sulphate and concentrated HCl, and HBr respectively (B. **37,** 1861).

2, 4-Dinitro-benzaldehyde $(NO_2)_2[2, 4]C_6H_3CHO$, m.p. 72°, is obtained by the oxidation of 2, 4-dinitro-benzyl-aniline or its **sulphonic acid** $(NO_2)_2C_6H_3CH_2NHC_6H_4SO_3H$ with permanganate or chromic acid, the Schiff bases first formed being split up by the acid; it is also produced by the breaking up of its **dimethyl-amido-anile** $(NO_2)_2C_6H_3CH : NC_6H_4N(CH_3)_2$, obtained by the action of p-nitroso-dimethyl-aniline upon 2, 4-dinitro-toluol. From 2, 4, 6-trinitro-toluol we obtain in this manner the **2, 4, 6-trinitro-benzaldehyde** $(NO_2)_3[2, 4, 6]C_6H_2CHO$, m.p. 119°. Like the o-nitro-benzaldehyde, the o, p-dinitro- and the sym. trinitro-benzaldehyde are easily transposed by light into p-nitro-o-nitroso- and dinitro-o-nitroso-benzoic acid (B. **35,** 2704; **36,** 959; C. 1902, II. 741).

Hydroxylamino-, Nitroso-, Azoxy-, and Azo-benzaldehydes.—By electrolytic reduction in sulphuric acid, and by reduction with zinc dust, we obtain from m- and p-nitro-benzaldehyde in the first place aldehydo-phenyl-hydroxylamines $CHO.C_6H_4NHOH$, which, with unchanged nitro-aldehyde, combine to form aldehydo-phenyl-nitro-n-benzal-doximes $NO_2C_6H_4CH\langle^{NC_6H_4CHO}_{O}$. The o-nitro-benzaldehyde may be reduced to the very unstable hydroxylamino-benzaldehyde, which is easily condensed to its inner anhydride *anthranile.* In the form of its *nitroso-compound* $CHO.C_6H_4N(NO)OH$, m.p. 52·5°, we obtain **o-hydroxylamino-benzaldehyde** by reducing o-nitro-benzaldehyde with zinc dust in the presence of amyl nitrite (B. **42,** 2574). The same nitroso-compound also results from anthranile with HNO_2. With alkalies it gives stable salts, while with acids it is converted into a mixture of diazotised o-amido-benzaldehyde and **o-nitroso-benzaldehyde** CHO [1]C_6H_4[2]NO, white needles of m.p. 110° (B. **42,** 2573).

o-Hydroxylamino-benzaldoxime $HONH[2]C_6H_4CH : NOH$, m.p. 120°, is formed by reduction of o-nitro-benzaldoxime. This oxime is also formed from anthranile with hydroxylamine, and is reconverted into anthranile by acids. By oxidation, in air, it passes into the oxime of **2-azoxy-benzaldehyde** $ON_2(C_6H_4[2]CHO)_2$, m.p. 211° (B. **36,** 3654). The aldehyde melts at 119°; it is more easily obtained by the reduction of o-nitro-benzaldehyde acetic acid splitting (B. **39,** 4265). On a peculiar reduction product of **o-nitro-benzaldehyde** $C_{14}H_{12}N_2O_5$, m.p. 99°, which reacts like a molecular combination of o-nitro- and o-hydroxyl-amino-benzaldehyde, see B. **39,** 4252. By a further reduction of m- and p-nitro-benzaldoxime-n-aldehydo-phenol ether, we obtain the corresponding derivatives of azoxy-benzaldoximes, which are split up by ferric chloride into the **azoxy-benzaldehydes** $ON_2(C_6H_4CHO)_2$, m m.p. 129°, p- m.p. 190°, and **nitroso-benzaldehydes** $NO.C_6H_4.CHO$. p-Azoxy-benzaldehyde is also obtained in the form of its *aniline compound* $ON_2(C_6H_4CH : NC_6H_5)_2$ from **p-nitro-benzyl-aniline** $NO_2C_6H_4CH_2NHC_6H_5$ by the action of potash (see also B. **36,** 3469). p-Nitroso-benzaldehyde combines with aniline to form the **anile** of **p-benzol-azo-benzaldehyde** $C_6H_5N : NC_6H_4CHO$, m.p. 120°, whose acetal is also pro-

duced by the reduction of a mixture of nitro-benzol and p-nitro-benzaldehyde alcohol, beside the acetal of **p-azo-benzaldehyde** $CHO.C_6H_4N : NC_6H_4CHO$, m.p. 238° (B. **35**, 2434; **36**, 793; C. 1902, II. 195, 700; 1903, I. 286). **o-** and **m-azo-benzaldehyde-acetal,** m.p. 144° and 150°, are formed by reduction of the nitro-benzaldehyde acetals with zinc dust and sodium hydrate (C. 1904, I. 1498). The o-azo-benzaldehyde-acetal yields on saponification with dilute SO_4H_2 *γ-oxy-β-phenyl-indazol* $C_6H_4<\overset{C(OH)}{\underset{N}{\cdot}}>NC_6H_5$ (C. 1907, I. 1575).

Amido-benzaldehydes $NH_2C_6H_4CHO$. The o- and p-bodies are obtained in the action of ferric chloride upon their oximes, which are formed by the reduction of o- and p-nitro-benzaldoximes with ammonium sulphide (B. **15**, 2004; **16**, 1998).

o-Amido-benzaldehyde is also obtained by reducing o-nitro-benzaldehyde and *anthranile* (see this) with ferrous sulphate and ammonia (B. **17**, 456). m-Amido-benzaldehyde is formed when m-nitro-benzaldehyde is reduced with tin and glacial acetic acid.

A further process for preparing o- and p-amidated benzaldehydes uses the action of sulphur alkalies upon nitro-benzyl alcohols and their derivatives; a reduction of the nitro-group and an oxidation of the alcohol group takes place (C. 1900, I. 1084).

o-Amido-benzaldehyde . . melts at 39°: its *oxime* at 135° (B. **36**, 803)
m-Amido-benzaldehyde is yellow and amorphous; „ 88°
p-Amido-benzaldehyde . . melts at 70°: „ 124° (*J. pr. Ch.* **2**, **56**, 97).

For preparing the derivatives of the amido-benzaldehydes, very unstable in themselves, their acetyl derivatives are specially suitable. Their melting-points are: o-, 71°; m-, 84°; and p-, 161° (C. 1903, I. 775, 921).

p-Dimethyl- and *p-diethyl-amido-benzaldehydes*, melting at 73° and 81°, are obtained when the condensation products from chloral and dialkyl-aniline — *e.g.* p-dimethyl-amido-phenyl-trichlorethyl alcohol $(CH_3)_2NC_6H_4CH(OH)CCl_3$—are acted upon with alcoholic potash (B. **19**, 365). p-Dimethyl-amido-benzaldehyde condenses to *hexamethyl-leucaniline* (see Triphenyl-methane dyes) with dimethyl-aniline.

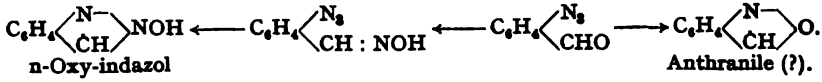
For further condensation products of p-dimethyl-amido-benzaldehyde, see B. **35**, 3569.

Tetramethyl-2, 4-diamido-benzaldehyde, m.p. 8°, $b.p._{14}$ 203°, from tetramethyl-m-phenylene-diamine and chloral (B. **41**, 91).

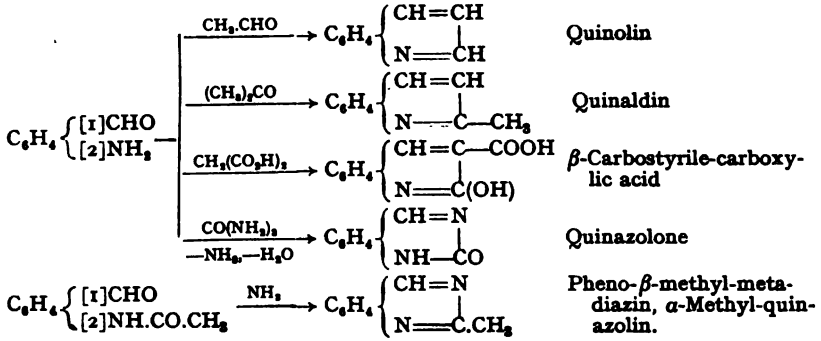
The o-amido-benzaldehyde is easily diazotated with concentrated HCl; on treating the diazonium salt with sodium nitride we obtain **o-azido-benzaldehyde** $\overset{N}{\underset{N}{>}}N[2]C_6H_4CHO$, m.p. 37°. This body is also produced by a peculiar transposition of the **diazo-benzaldoxime anhydride,** *indiazonoxime*, $\overline{N : N[2]C_6H_4C} : NOH$, m.p. 166°, formed during the diazotation of o-amido-benzal-dioxime, performed by warming in water, or treating with cold alkali. The same reactions have been carried out with dimethyl-, dichloro-, and dibromo-o-amido-benzaldehyde.

o-Azido-benzaldehyde, on heating alone, or with water, loses nitrogen, and passes into anthranile. A similar behaviour is shown

by the **o-azido-benzaldoxime** $N_3[2]C_6H_4CH:NOH$, m.p. 103°, which, on boiling with NaHO, gives **n-oxy-indazol** (B. **35,** 1885) :



The Hetero-ring Formations of o-Amido-benzaldehyde.—o-Amido-benzaldehyde combines especially readily with compounds containing a CH_2–CO group, in the presence of dilute caustic soda. The products resulting at first are of an aldol nature, for they immediately split off water and yield quinolin or its derivatives. o-Amido-benzaldehyde combines with acetaldehyde to *quinolin*, with acetone to *quinaldin*, with malonic acid to *β-carbostyrile-carboxylic acid* (B. **25,** 1752), and with urea to *quinazolone* (B. **28,** 1037). Alcoholic ammonia transposes the acidyl-o-amido-benzaldehydes into quinazolins :



On the condensation of o-amido-benzaldehyde by means of zinc chloride to anhydro-o-amido-benzaldehyde $(C_7H_6N)_x$, see B. **31,** 658.

Benzaldehyde-m-sulphonic acid $SO_3H.C_6H_4CHO$, white deliquescent crystals (B. **24,** 791). **Benzaldehyde-o-sulphonic acid** is obtained from o-chloro-benzaldehyde with sodium sulphite, as well as by oxidation of o_2-stilbene-disulphonic acid. The chloride, m.p. 114°, treated with NH_3 and then oxidised in air, yields *saccharin* (C. 1898, I. 540 ; 1901, I. 806). Benzaldehyde-mono- and -disulphonic acids are also produced by oxidation of toluol-sulphonic acids with MnO_2 and fuming sulphuric acid (C. 1904, II. 1269).

(3) Aromatic Monoketones.

The oxidation products of the secondary phenyl-paraffin alcohols are *mixed ketones*, in which an aromatic and an aliphatic hydrocarbon residue are joined by the CO group. The ketones containing two benzene residues linked by carbonyl, such as benzo-phenone or diphenyl-ketone, will be discussed later in connection with the corresponding hydrocarbons, like diphenyl-methane.

Formation.—Mixed aromatic-aliphatic ketones are usually produced by reactions similar to those employed with the aliphatic ketones :

(1) By the oxidation of secondary alcohols, like phenyl-methyl carbinol.

(2*a*) From the di-secondary and secondary-tertiary phenyl-ethylene

glycols and ethylene oxides by heating with dilute acids or alone (C. 1905, II. 1628; 1907, I. 1577):

$$C_6H_5CH(OH).CH(OH)CH_3 \longrightarrow C_6H_5CH_2.CO.CH_3 \longleftarrow C_6H_5\overline{CH.O.CH}.CH_3.$$

(2*b*) From the iodo-hydrins of some olefin-benzols on treating with NO_3Ag or HgO, with migration of the phenyl group:

$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}\!\!>\!C(OH).CHI.CH_3 \longrightarrow CH_3.CO.CH\!<\!\begin{matrix} C_6H_5 \\ CH_3 \end{matrix}.$$

(3) When sulphuric acid acts upon phenyl-acetylene:

$$C_6H_5C : CH \longrightarrow C_6H_5COCH_3.$$

Nuclear Synthesis.—(4) By the distillation of a mixture of calcium salts of an aromatic and a fatty acid (C. 1910, I. 1008).

(5) By the action of zinc alkyls on acid chlorides (A. **118**, 20).

(6) By the action of alkyl-magnesium iodides upon aromatic nitriles addition products are obtained, which, on decomposition with mineral acids, give aromatic ketones (C. 1902, I. 299):

$$C_6H_5C{\equiv}N + CH_3MgI \longrightarrow C_6H_5C\!<\!\begin{matrix} CH_3 \\ NMgI \end{matrix} \longrightarrow C_6H_5COCH_3.$$

Benzo-nitrile oxide $C_6H_5.C\!<\!\begin{matrix} N \\ O \end{matrix}$ with alkyl-magnesium haloids gives ketoximes (B. **40**, 1672).

(7) From benzols by the action of aliphatic acid chlorides and Al chloride or ferric chloride. Additive compounds of these chlorides and the acid chlorides are first formed, *e.g.* $(CH_3COCl)AlCl_3$, and these thereupon react with the hydrocarbons (B. **88**, 815; C. 1900, II. 188; 1901, I. 1263).

(8) By heating aryl-glycidic acids. These are easily obtained synthetically by condensing aromatic aldehydes or ketones with α-chloro-propionic ester and sodium ethylate (C. 1906, I. 669):

$$C_6H_5COCH_3 \longrightarrow C_6H_5(CH_3)\overline{C.O.CH}COOH \longrightarrow C_6H_5(CH_3)CHCO.CH_3.$$

(9) From aldehydes with diazo-methane (B. **40**, 479).

(10) In the alkyl-phenyl ketones the H atoms adjoining the carboxyl group may be replaced by alkyls by the action of sodium amide and halogen alkyls (C. 1909, I. 647; II. 600):

$$C_6H_5COCH_2CH_3 \xrightarrow[NaNH_2]{C_2H_5I} C_6H_5CO.C(C_2H_5)_2CH_3.$$

(11) By decomposing β-ketone-carboxylic acids—*e.g.* mono- and dialkyl-benzoyl-acetic acids (B. **16**, 2131)—with alcoholic potash.

(12) Acidulated benzols finally result, as a consequence of intramolecular rearrangement, upon heating the alkyl ethers of phenyl-olefin alcohols, which are prepared by the distillation of ortho-ethers of aceto-phenone. In this way the acidyl benzols can be built up from aceto-phenone (Claisen, B. **29**, 2931):

$$C_6H_5CO.CH_3 \longrightarrow C_6H_5C(OCH_3)_2.CH_3 \longrightarrow C_6H_5C(OCH_3) : CH_2 \longrightarrow C_6H_5COCH_2.CH_3$$

Aceto-phenone and higher ketones are found in the so-called heavy benzene oil of coal-tar (B. **86**, 754).

Properties and Behaviour.—The mixed aromatic-aliphatic ketones are colourless liquids, insoluble in water, and possess an odour which is not disagreeable.

(1) On reduction they pass into secondary alcohols or the corresponding alkyl-benzols (C. 1905, I. 29).

(2*a*) Chromic acid transforms the ketone $C_6H_5.COR$ into benzoic acid and the alkyl, which is further oxidised.

(2*b*) Potassium permanganate converts them into α-ketone-carboxylic acids (B. **23,** R. 640; **24,** 3543; **26,** R. 191).

(3) Acids and acid amides, with the same number of carbon atoms, strangely enough, are formed when phenyl-alkyl ketones are heated with yellow ammonium sulphide (*J. pr. Ch.* 2, **81,** 74, 382):

$$C_6H_5COCH_2CH_3 \begin{cases} \longrightarrow C_6H_5CH_2CH_2CO_2H \\ \longrightarrow C_6H_5CH_2CH_2CONH_2 \end{cases}.$$

With increasing number of carbon atoms in the side chain, the yield of carboxylic acids decreases, so that it vanishes in phenyl-heptyl ketone.

(4) On heating benzene ketones with sulphuric acid, the acetyl group splits off, and benzol-sulphonic acid results (B. **19,** 2623).

(5) Those ketones in which the CO group is attached to the benzene nucleus *do not* unite with alkaline bisulphites.

(6) The phenyl-alkyl ketones apparently form but *one* acetoxime with hydroxylamine; the opposite is true of benzaldehyde.

(7) They form *hydrazones* with phenyl-hydrazin.

(8) With phosphoric and arsenic acids the aryl-methyl ketones especially form crystalline compounds, some of which, when heated, regenerate the hydrocarbons with elimination of the keto-group (B. **32,** 1549; **35,** 2313).

(9) On heating with sodium amide in benzene solution, the trialkyl-aceto-phenones break up into benzene and the amides of the corresponding trialkyl-acetic acids (C. 1909, I. 912; II. 600):

$$C_6H_5CO.C(CH_3)_3 \xrightarrow{NaNH_2} C_6H_6 + NH_2CO.C(CH_3)_3.$$

Aceto-phenone, *phenyl-methyl ketone, acetyl-benzol* $C_6H_5.CO.CH_3$, m.p. 20°, b.p. 202°, crystallises in large plates. It is applied as an opiate under the name of *hypnone.* It is formed (1) from phenyl-methyl carbinol; (2) from phenyl-acetylene; (3) by distilling benzoate of calcium with calcium acetate; (4) by the action of zinc methyl upon benzoyl chloride; (5) from benzene, acetyl chloride, and $AlCl_3$; (6) from benzaldehyde and diazo-methane; (7) from benzoyl-aceto-acetic ester $C_6H_5CO.CH(COCH_3).COOC_2H_5$ and benzoyl-acetic ester. The methods 3 and 5 are employed in its preparation.

Nascent hydrogen converts it readily into phenyl-methyl carbinol. Chromic acid oxidises it to benzoic acid, and potassium permanganate to phenyl-glyoxylic acid.

Aceto-phenone, like acetone, has been introduced into numerous nuclear-synthetic reactions. Some of the simplest of these will be given. It may be condensed to *dypnone* (*q.v.*) and to [1, 3, 5]-*triphenyl-benzol* (cp. C. 1900, II. 255), two bodies bearing the same relation to aceto-phenone that mesityl oxide and mesitylene have to acetone.

Aceto-phenone also condenses in the most varied proportions with benzaldehyde, forming benzal-aceto-phenone, benzal-diaceto-phenone, and dibenzal-triaceto-phenone (B. **29,** 1488). It yields the nitrile of α-phenyl-lactic acid with hydrocyanic acid. At higher temperatures

chlorine enters the methyl group; PCl_5 substitutes the ketone-oxygen-producing **aceto-phenone chloride** (A. **217**, 105). Amyl nitrite and sodium ethylate convert aceto-phenone into *iso-nitroso-aceto-phenone*, which will be described under *Phenyl-glyoxal*.

With ammonia, aceto-phenone reacts like the higher aliphatic ketones, with formation of **aceto-phenone ammonia** $(C_6H_5(CH_3)C)_2N_2$, m.p. 115° (C. 1907, I. 809).

Ortho-ethers of aceto-phenone, like **aceto-phenone ortho-ethyl ether** $C_6H_5C(OC_2H_5)_2CH_3$, b.p. 107° (17 mm.), are prepared from aceto-phenone and ortho-formic ethers (B. **40**, 3908). When heated under ordinary pressure, or by the action of acid chlorides and pyridin (B. **31**, 1019), they lose alcohol and pass into alkyl ethers of phenyl-olefin alcohols. They yield aniles with aniline. **Aceto-phenone-anile** $C_6H_5C:(NC_6H_5)CH_3$, m.p. 41°, b.p. 310°.

Aceto-phenone-ethyl mercaptol $C_6H_5C(SC_2H_5)_2CH_3$ is oxidised by permanganate, in the cold, to the disulphone $C_6H_5C(SO_2C_2H_5)_2CH_3$, m.p. 120° (B. **35**, 2343).

Aceto-phenone oxime $C_6H_5.C:(N.OH).CH_3$, m.p. 59°. It is only known in one modification (B. **24**, 3482). By the action of concentrated sulphuric acid, or of HCl in glacial acetic acid, it is converted into acetanilide $C_6H_5.NH.CO.CH_3$. This remarkable intramolecular atomic rearrangement was discovered by Beckmann ("Beckmann's Transposition," B. **20**, 2580; **23**, 2746).

Other ketoximes behave in an analogous manner. The reaction has been applied in determining the point of double union in the higher olefin-monocarboxylic acids, and for the decomposition, or rupture, of ring ketones.

Aceto-phenone-phenyl-hydrazone melts at 105°.

Aceto-phenone Homologues.—These are numerous, and can be arranged in two groups: (A) ketones whose CO group is attached to the benzene ring—**acidulated benzols**; (B) ketones whose CO group is not in immediate union with the benzene ring—**phenylated fatty ketones.**

(A) **Acidulated benzols** have been made, especially by the general methods 4, 6, 7, 10, 11, 12.

Benzoylated paraffins:

Propio-phenone	$C_6H_5COCH_2CH_3$	b.p. 210°[1]
Butyro-phenone	$C_6H_5CO(CH_2)_2CH_3$	,, 222°
Valero-phenone	$C_6H_5CO(CH_2)_3CH_3$	,, 237°
Iso-valero-phenone	$C_6H_5CO.CH_2CH(CH_3)_2$	,, 230°
Tert. butyl-phenyl ketone	$C_6H_5CO.CH(CH_3)_2$	,, 220°[2]
Caprono-phenone	$C_6H_5CO(CH_2)_4CH_3$	b.p.$_{14}$ 133°[3]
Iso-amyl-phenyl ketone	$C_6H_5COCH_2.CH_2CH(CH_3)_2$	b.p. 240°
Diethyl-aceto-phenone	$C_6H_5COCH(C_2H_5)_2$	,, 230°[4]
Ethyl-dimethyl-aceto-phenone	$C_6H_5COC(CH_3)_2C_2H_5$	b.p.$_{10}$ 112°[4]
Hexyl-phenyl ketone	$C_6H_5CO(CH_2)_5CH_3$	b.p.$_{15}$ 115°
Propyl-dimethyl-aceto-phenone	$C_6H_5COC(CH_3)_2C_3H_7$	b.p.$_{10}$ 112°[4]
Triethyl-aceto-phenone	$C_6H_5COC(C_2H_5)_3$	b.p.$_{10}$ 145°[4]
Lauroyl-benzol	$C_6H_5CO(CH_2)_{10}CH_3$	m.p. 47°[5]
Palmityl-benzol	$C_6H_5CO(CH_2)_{14}CH_3$	,, 59°

Literature.—[1] B. **26**, 1427; **35**, 1073. [2] A. **310**, 318. [3] B. **40**, 1601. [4] C. 1909, I. 647. [5] B. **28**, R. 648.

Benzoyl-trimethylene $C_6H_5CO.CH\langle\begin{matrix}CH\\|\\CH_2\end{matrix}$, formed on heating trimethylene-benzoyl-acetic acid to 200°, boils at 239°. Its *oxime* melts at 88°.

Benzoyl-tetramethylene $C_6H_5COCH\langle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle CH_2$, from the chloride of tetramethylene-carboxylic acid, boils at 258° (B. **25**, R. 372).

Nuclear-acidulated Alkyl-benzols, Homobenzoylated Paraffins. — p-Acetyl-toluol is produced when concentrated nitric acid acts upon cymene (pp. 58), and acetyl-3, 4-(o)-xylol is formed from camphor by the action of concentrated sulphuric acid (B. **26**, R. 415) :

p-Acetyl-toluol $CH_3CO[4].C_6H_4[1].CH_3$	boils at	224°	
1-Acetyl-3, 4-(o)-xylol	„	246°	
1-Acetyl-2, 4-(m)-xylol	„	247°	
Acetyl-p-xylol	„	224°	
Acetyl-mesitylol	„	235° (B. **24**, 3542)	
1-Acetyl-2, 4, 5, 6-durol	melts at 73° and	„	206° (B. **29**, 847).

(B) **Phenylated fatty ketones** have been prepared by methods 2, 4, 5, 6, 8, and 11 (p. 264 *seq.*) :

Benzyl-propyl ketone $C_6H_5CH_2.CO.CH_2CH_3$, b.p. 240°, from benzyl cyanide with propyl-magnesium iodide, etc. (C. 1902, I. 299).

Benzyl-methyl-ethyl ketone $C_6H_5CH_2CH_2COCH_2CH_3$, b.p. 257°, from α-benzylidene-methyl-ethyl ketone by reduction, or by distillation of calcium hydro-cinnamate or propionate (B. **35**, 971).

Substituted Aceto-phenones.— *Haloid Aceto-phenones.* — Aceto-phenones containing halogens in the methyl group will be discussed after the corresponding oxygen derivatives : *benzoyl-carbinol* (*q.v.*), *phenyl-glyoxal* (*q.v.*), and *phenyl-glyoxylic acid* (*q.v.*). p-Haloid aceto-phenones, like $Cl.C_6H_4.CO.CH_3$, have been obtained from haloid benzenes, acetyl chloride, and aluminium chloride (cp. haloid thiophene ketones) (B. **24**, 997, 3766) :

p-Chloraceto-phenone, *acetyl-p-chloro-benzene,* melts at 20° and boils at 230° (B. **18**, R. 502).

p-Bromaceto-phenone, *acetyl-p-bromo-benzene,* melts at 51°.

p-Iodaceto-phenone, *acetyl-p-iodo-benzene,* melts at 83°.

Nitro-aceto-phenones.—The meta-body is the chief product (just as in the case of benzaldehyde) when aceto-phenone is dissolved in fuming nitric acid ; at 30°–40° o-nitro-aceto-phenone predominates (B. **18**, 2238). The three isomerides can be prepared from the three nitro-benzoyl-aceto-acetic esters (see these) (A. **221**, 323).

p-Nitro-aceto-phenone is formed when concentrated sulphuric acid acts upon p-nitro-phenyl-propiolic acid (see this), through the rearrangement of the nitro-phenyl-acetylene, formed at first, by water (A. **212**, 160) (see method of formation 3).

o-Nitro-aceto-phenone, b.p.$_{16}$ 159° ; *oxime,* m.p. 115° (C. 1902, I. 472)
m-Nitro-aceto-phenone, m.p. 81° ; „ „ 131° (B. **87**, 3542)
p-Nitro-aceto-phenone, „ 80°.

o-Nitro-aceto-phenone oxime is also produced from o-nitro-ethyl-benzol $NO_2C_6H_4CH_2CH_3$ with amyl nitrite and sodium ethylate (see Nitro-benzaldoximes, and C. 1900, II. 458).

m-Dinitro-aceto-phenone, m.p. 83°, is prepared from dinitro-benzoyl-aceto-acetic ester with H_2SO_4 (*J. pr. Ch.* 2, **65**, 290).

o-Nitro-aceto-phenone, on gentle reduction with zinc dust and sal ammoniac or tin and acetic acid, is converted into **o-hydroxylamino-aceto-phenone anhydride** or **o-methyl anthranile** $C_6H_4\begin{cases}C(CH_3)\\ N\end{cases}O$, b.p.$_{10}$ 111°, a colourless oil, easily volatilised with steam, which must be regarded as analogous to anthranile; like the latter, it forms with sublimate a double compound, which, on further reduction, passes into amido-aceto-phenone. On heating at ordinary pressure it is transposed into indoxyl or converted into indigo (see Indigo syntheses, and B. **86**, 1611).

m-Hydroxylamino-, azoxy- and **azo-aceto-phenones**, see B. **86**, 1618; C. 1903, II. 112.

Amido-aceto-phenones $C_6H_4(NH_2).CO.CH_3$.

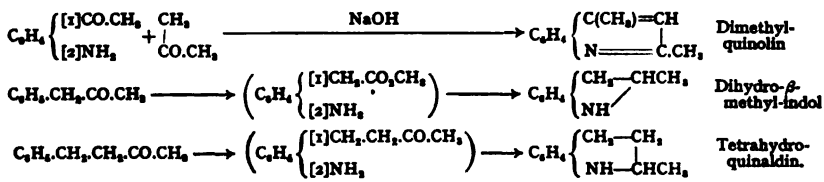
o-, m- and **p-Amido-aceto-phenone** are obtained: by reducing o-nitro-aceto-phenone (A. **221**, 326); the o-amido-aceto-phenone has also been prepared from o-amido-phenyl-propiolic acid by boiling in water (B. **15**, 2153); from o-amido-phenyl-acetylene $C_6H_4(NH_2)C:CH$ by the action of sulphuric acid (B. **17**, 964); by boiling o-amido-phenyl-propiolic acid with water (B. **15**, 2153); and a slight quantity on heating aniline with acetic anhydride (B. **18**, 2688). **o-Amido-aceto-phenone** is a thick yellow oil, which boils at 242°–252°, and possesses a characteristic sweetish odour. **m-Amido-aceto-phenone** melts at 93°. **p-Amido-aceto-phenone** melts at 106°; its *oxime* melts at 147° (B. **20**, 512). A pine splinter dipped into the aqueous solution of o-amido-aceto-phenone hydrochloride is coloured an intense orange-red.

o-, m- and **p-Acetyl-amido-aceto-phenones** $CH_3CONHC_6H_4COCH_3$, m.p. 77°, 129°, and 167°. The p-body is also formed from diacet-anilide by transposition on heating with HCl or zinc chloride (C. 1903, I. 832).

Hetero-ring Formations of the Aromatic o-Amido-ketones.—(1) Dimethyl-quinolin is produced (B. **19**, 1037) when o-amido-aceto-phenone is digested with acetone and sodium hydroxide.

(2) o-Acetyl-amido-aceto-phenone is condensed by NaHO to α-methyl-γ-oxy- and α-oxy-γ-methyl-quinolin (B. **32**, 3228).

(3) and (4) Oily nitro-compounds are formed in the nitration of phenyl-acetone and benzyl-acetone. They yield, by reduction, β-methyl-dihydro-ketol and tetrahydro-quinaldin (B. **14**, 889), as the o-amido-bodies (probably the o-amido-alcohols) produced at first sustain an intramolecular anhydride formation:



(4) Aromatic Monocarboxylic Acids.

The aromatic carboxylic acids result upon replacing the hydrogen in benzene or its homologues by the carboxyl group. This group in

these new derivatives is directly linked, as in the benzene-carboxylic acids, to the benzene ring, or it replaces the hydrogen of an alkyl side chain :

$C_6H_5.CO_2H$ Benzoic acid	$C_6H_4(CO_2H)_2$ Phthalic acids	$C_6H_3(CO_2H)_3$ . . . Benzene-tricarboxylic acids	$C_6(CO_2H)_6$ Mellitic acid
$CH_3.C_6H_4CO_2H$ Toluic acids	$(CH_3)_2C_6H_3CO_2H$ Xylic acids	$C_6H_5CH_2CO_2H$ Phenyl-acetic acid *α*-Toluic acid	$C_6H_5CH_2CH_2CO_2H$ Hydro-cinnamic acid *β*-Phenyl-propionic acid.

Only the monocarboxylic acids will be now discussed, after the monohydric aromatic alcohols.

General Methods of Formation.—(1) While the aliphatic monocarboxylic acids or the paraffin carboxylic acids could not be obtained by the oxidation of the paraffins, the aromatic acids can be readily obtained from the benzene homologues by oxidising the side chains to carboxyl groups. The importance of this reaction in establishing constitution has been previously alluded to (p. 54). The most suitable oxidants are chromic acid, dilute nitric acid, potassium permanganate, and potassium ferricyanide.

(*a*) *Oxidation with Chromic Acid.*—Only the *para-* and *meta-derivatives* (the former more readily than the latter) of benzenes, carrying two side chains, are oxidised to acids by chromic acid, while the ortho- are either not attacked at all, or are completely destroyed.

In substituted alkyl-benzenes the alkyl group is prevented from being oxidised by chromic acid, if a negative group occupying the o-position with reference to the alkyl group is present (B. **15**, 1021). The oxidations are conducted either with free chromic acid in glacial acetic acid, or with a mixture of potassium bichromate (3 parts) and sulphuric acid (3 parts), diluted with 2–3 volumes of water.

(*b*) *Oxidation with Nitric Acid.*—When oxidising with nitric acid, use acid diluted with 3 parts of water and boil for some time, in connection with a return condenser (2–3 days). Konowaloff contends that phenyl-nitro-paraffins are first produced ; these then are further oxidised to carboxylic acids. To remove the nitro-acids which are invariably formed, the crude product is digested with tin and concentrated hydrochloric acid ; this converts the nitro- into amido-acids, which dissolve in hydrochloric acid.

In the derivatives with two different alkyls the higher alkyl is usually attacked first, by nitric acid or chromic acid ; sometimes ketones are present in the intermediate products (see Cymol, p. 58).

(*c*) Potassium permanganate often effects the oxidation at ordinary temperatures. Ortho-di-derivatives may also be subjected to oxidation, without the complete destruction of the benzene nucleus following as a consequence.

(*d*) Potassium ferricyanide oxidises methyl to carboxyl, if the nitro-group occupies the ortho-position relatively to the methyl group. This does not occur if the nitro-group holds the meta-position (B. **22**, R. 501).

(2) Oxidation of the corresponding aromatic alcohols and aldehydes.

(3) By the addition of hydrogen to the unsaturated monocarboxylic acids. Cinnamic acid becomes hydro-cinnamic acid.

(4) By the reduction of phenylated oxy-fatty acids, haloid aromatic acids, and ketone-carboxylic acids.

(5) From the phenyl-alkyl ketones by heating with Am_2S, acids and acid amides of the same number of C atoms are produced :

1. $C_6H_5.CH_3 \xrightarrow{3O} C_6H_5COOH$
2. $C_6H_5.CH_2OH \longrightarrow C_6H_5CHO \longrightarrow C_6H_5COOH$
3. $C_6H_5.CH{=}CH.COOH \xrightarrow{2H} C_6H_5CH_2.CH_2.COOH$
4. $C_6H_5.CH(OH).COOH \xrightarrow{2HI} C_6H_5CH_2.COOH$
   $C_6H_5.CO.CO_2H \xrightarrow{4HI} C_6H_5CH_2.COOH$
   $C_6H_5.CHCl.COOH \xrightarrow{2H} C_6H_5CH_2COOH$
5. $C_6H_5.CO.CH_2.CH_3 \xrightarrow{(NH_4)_2S} C_6H_5CH_2.CH_2.COOH.$

Nuclear-synthetic Reactions.—(6*a*) Action of CO_2 upon aryl-magnesium haloids; phenyl-magnesium iodide gives rise to benzoic acid, and benzyl-magnesium chloride to phenyl-acetic acid.

(6*b*) Action of sodium and CO_2 upon monobromo-benzols (Kekulé).

(7) A similar reaction is that of sodium and esters of chloro-carbonic acid upon phenols and bromo-hydrocarbons (Würtz).

(8) Fusion of salts of the sulphonic acids with sodium formate.

(9) Action of carbon oxy-chloride upon benzols in the presence of Al chloride, acid chlorides being obtained.

(10) Urea chlorides, in the presence of $AlCl_3$, act in an analogous manner upon the benzols. Acid amides are the first products. The urea chlorides can be replaced (*a*) by cyanuric acid, or (*b*) by nascent cyanic acid and HCl (B. **82**, 1116); (*c*) with phenyl cyanate we obtain anilides; (*d*) with phenyl-mustard oil we get thio-anilides (*J. pr. Ch.* 2, **59**, 572).

(11) By the action of benzene and aluminium chloride upon aliphatic lactones or olefin-carboxylic acids (C. 1908, II. 1100).

(12) By the synthesis of the acid nitriles :

(*a*) Upon fusing the sulphonates with potassium cyanide;

(*b*) By action of potassium cyanide upon the phenyl-alkyl chlorides;

(*c*) When the bromo-nitro-benzols are heated with potassium cyanide;

(*d*) When diazo-salts are treated with potassium cyanide and copper sulphate;

(*e*) By heating the iso-nitriles alone.

The nitriles are changed to carboxylic acids when they are heated with mineral acids, or alkalies.

Nuclear Syntheses :

6. $C_6H_5MgI+CO_2 \longrightarrow C_6H_5COOMgI$
7. $C_6H_5Br+ClCO_2C_2H_5+2Na \longrightarrow C_6H_5COOC_2H_5+NaCl+NaBr$
8. $C_6H_5SO_3Na+HCOONa \longrightarrow C_6H_5COONa+HSO_3Na$
9. $C_6H_6+COCl_2 \xrightarrow{Al_2Cl_6} C_6H_5COCl+HCl$
10*a*. $C_6H_6+Cl.CONH_2 \xrightarrow{Al_2Cl_6} C_6H_5CONH_2+HCl$
   b. $C_6H_6+CO:NH \xrightarrow{+HCl} C_6H_5CONH_2$

10*c*. $C_6H_6+CO:NC_6H_5 \xrightarrow{Al_2Cl_6} C_6H_5CONHC_6H_5$

d. $C_6H_6+CS:NC_6H_5 \xrightarrow{Al_2Cl_6} C_6H_5CSNHC_6H_5$

11. $C_6H_6+CH_3CH:CH.COOH \xrightarrow{Al_2Cl_6} C_6H_5(CH_3)CH.CH_2COOH$

12*a*. $C_6H_5SO_3K+CNK \longrightarrow C_6H_5CN+SO_3K_2$

b. $C_6H_5CH_2Cl+CNK \longrightarrow C_6H_5CH_2CN+KCl$

c. $C_6H_4BrNO_2+CNK \longrightarrow C_6H_4(NO_2)CN+KBr$

d. $C_6H_5N_2Cl+CNK \longrightarrow C_6H_5CN+N_2+KCl$

e. $C_6H_5.NC \longrightarrow C_6H_5CN.$

(13) By the oxidation of phenyl-pyro-racemic acids with hydrogen peroxide (A. **370**, 368):

$$C_6H_5CHO \longrightarrow C_6H_5CH_2.COCOOH \longrightarrow C_6H_5CH_2COOH.$$

(14) Action of benzyl chloride upon sodium-aceto-acetic ester, and the decomposition of the ketonic esters—*e.g.* benzyl-aceto-acetic ester—by alkalies.

(15) The decomposition of phenyl substitution products of the malonic acid series—*e.g.* benzyl-malonic acid—by heat.

(16) Action of metallic sodium upon the acetates, propionates, etc., of the phenyl carbinols: benzyl acetate yields phenyl-propionic benzyl ester, while β-benzyl-phenyl-butyric ester is obtained from benzyl propionate. This reaction recalls the synthesis of aceto-acetic ester (Vol. I.), inasmuch as, in the latter, alcohol is split off under the influence of sodium, while, in the present reaction, acetic acid is liberated:

$C_2H_5OOCCH_2\boxed{H}$ $\quad$ $C_6H_5CH_2OOC.CH_2\boxed{H}$

$CH_3CO\ \boxed{OC_2H_5}$ $\quad$ $C_6H_5CH_2\boxed{OOCCH_3}$

Aceto-acetic ester $\quad$ **β-Phenyl-propionic benzyl ester.**

Besides these, unsaturated acids are formed by secondary reactions, leading, *e.g.*, to phenyl-acrylic acid and phenyl-crotonic acid (A. **198**, 321; **204**, 200):

$$\begin{matrix}COOCH_2C_6H_5\\ CH_2CH_2C_6H_5\end{matrix} + Na = \begin{matrix}COONa\\ CH:CHC_6H_5\end{matrix} + C_6H_5CH_3 + H.$$

Occurrence, Properties, and Behaviour.—The aromatic acids occur naturally, partly in a free state, partly in many resins and balsams, and in the animal organism (see Benzoic acid). They arise also in the decay of albuminoid bodies (see Hydro-cinnamic acid) (B. **16**, 2313).

The aromatic acids are crystalline solids, which generally sublime undecomposed. Most of them dissolve with difficulty in water; hence they are precipitated from their salt-solutions by mineral acids. Electrolytic reduction (B. **39**, 2933; **41**, 4148), or sodium amalgam, or zinc dust will reduce some to aldehydes, while heating with concentrated hydro-iodic acid, or phosphonium iodide, converts them into hydrocarbons. When heated with lime, or soda-lime, their carboxyl groups are eliminated and hydrocarbons result (cp. methane, Vol. I.).

From the polycarboxylic acids we obtain, as intermediate pro-

ducts, acids having fewer carboxyl groups—*e.g.* phthalic acid first yields benzoic acid and then benzene.

The hydrogen of the benzene nucleus in the acids can sustain substitutions similar to those observed with the hydrocarbons and phenols by the halogens, and the groups NO_2, SO_3H, NH_2, OH, etc. In other respects they are very similar to the fatty acids, and afford corresponding derivatives by the alterations of the carboxyl group.

Benzoic acid, *phenyl-formic acid* $C_6H_5.COOH$, m.p. 120° and b.p. 250°, occurs free in some resins, especially in gum benzoïn (from *Styrax benzoïn*), in dragon's blood (from *Dæmonorops Draco*), also in Peru and tolu balsams, where it exists in the form of its benzyl ester. It is found as hippuric acid in the urine of herbivoræ.

It is produced by the general methods 1 and 2 from toluol (B. **36,** 1798), benzyl alcohol, and benzaldehyde upon oxidation, as well as from all hydrocarbons, alcohols, aldehydes, ketones, and carboxylic acids, and their derivatives, which are obtainable from benzene by the replacement of *one* hydrogen atom by a univalent side chain. Benzoic acid can also be prepared by the oxidation of pure benzene; this is very probably due to the oxidation of diphenyl, which is formed at first (A. **221,** 234). Toluol can also be changed to benzyl chloride, and this can then be oxidised (see "Preparation") to benzoic acid; or benzotrichloride may be heated with water, concentrated sulphuric acid, or anhydrous oxalic acid, and the product will be benzoic acid. It can also be obtained, by the nuclear-synthetic reactions 6, 7, 8, 9, 10, and 12, from benzol, bromo-benzol, sodium-benzol sulphonate, and from aniline through diazo-benzol chloride or phenyl-carbylamine. Finally, CO_2 can be added to benzol by means of aluminium chloride, and benzoic acid will result.

History.—Benzoic acid was obtained from gum benzoïn by sublimation, in the beginning of the seventeenth century. In 1775 Scheele showed how the acid could be extracted from the gum with lime-water, and then be precipitated from the solution of its calcium salt. In 1832 Liebig and Wöhler, in the course of their classic research upon the radicle benzoyl, determined the elementary composition of the acid and illustrated its connection with benzaldehyde, as well as pointed out the simplest transformation products of the acid. This investigation produced such a profound impression upon the great master, Berzelius, that he proposed as a substitute for the name benzoyl—the name of the new radicle containing more than two elements—that of *proïn* or *orthrin*, from the Greek words, πρωί, the beginning of day, or ὄρθρος, morning dawn, because a new day was now breaking for organic chemistry. In 1834 Mitscherlich distilled benzoic acid with lime and got benzene, which led him to regard the acid as a derivative of this hydrocarbon. From that day, and especially since the establishment of the benzene theory by Aug. Kekulé, benzoic acid has been serving in constantly increasing amount as the fundamental material for the preparation of innumerable products. It is the carbon acid which has been most exhaustively investigated. The study of its derivatives has been greatly facilitated by the fact that the great crystallising power of the acid has been transferred to most of its compounds (Vol. I.).

Preparation.—Gum benzoïn is sublimed or the resin is boiled with milk of lime, and the benzoic acid precipitated with hydrochloric acid.

A more advantageous method is the production of the acid from hippuric acid. To accomplish this, boil the latter with concentrated hydrochloric acid. It is also produced when benzyl chloride is boiled with dilute nitric acid (B. **10,** 1275). Benzoic acid results from phthalic acid by heating its calcium salt to 350° with calcium hydroxide. For its preparation by hydrolysis of benzo-sulphonic acids, see C. 1899, I. 1173.

Properties and Behaviour.—Benzoic acid crystallises from hot water, in which it is very soluble, in white, shining flakes. It sublimes readily, and is carried over with steam. It dissolves with difficulty in cold water (1 part in 600 parts at 0°). Its vapours possess a peculiar odour, which produces coughing and sneezing. The officinal benzoic acid is obtained by the sublimation of Siam gum benzoïn.

The acid yields benzene and carbon dioxide when heated with lime. Benzoic acid, upon reduction, can yield *tetra-* and *hexahydro-benzoic acids* (*q.v.*).

Salts.—The *benzoates* are mostly quite readily soluble in water. Ferric chloride throws out a reddish precipitate of ferric benzoate from their neutral solutions.

The *potassium salt* $2C_7H_5KO_2+H_2O$ crystallises in concentrically grouped needles. The *calcium salt* $(C_7H_5O_2)_2Ca+3H_2O$ consists of shining prisms or needles. The *silver salt* $C_7H_5AgO_2$ crystallises from hot water in bright flakes. It dissolves in alcohol with great difficulty (B. **35,** 1094).

Homologues of Benzoic Acid.—These compounds, like the homologues of benzaldehyde and aceto-phenone, can be arranged in two groups: *alkyl-benzoic acids*, in which the CO_2H group is attached to the benzene nucleus, as in benzoic acid itself, and *phenyl-fatty acids*, in which the carboxyl group occurs in an aliphatic side chain of an alkyl-benzene. The first group or class is naturally more nearly related to benzoic acid than the second group.

Alkyl-benzoic acids.—*Toluic acids* or *methyl-benzoic acids* $CH_3.C_6H_4.CO_2H$ are isomeric with *α-toluic acid* or *phenyl-acetic acid*. They are produced when the three xylols are boiled for some time with dilute nitric acid, and from bromo- and iodo-toluol by the nuclear-synthetic methods 6 and 7, as well as from the three toluidins according to method 12*c*.

o-Toluic acid can also be obtained by the reduction of phthalide with hydriodic acid (B. **20,** R. 378), as well as by rupturing the ring of 1, 3-naphthalene-disulphonic acid, 1, 3-naphthalene derivatives, like 1, 3-dioxy-naphthalene, 1, 3-naphthalene-disulphonic acid, 1, 3-naphthol-sulphonic acid, upon fusing them with caustic alkali (B. **29,** 1611). p-Toluic acid is formed on boiling cymol with dilute nitric acid.

o-Toluic acid, m.p. 102°
m-Toluic acid, „ 110°, b.p. 263°
p-Toluic acid, „ 186°, „ 275°.

For derivatives of the toluic acids, see C. 1901, II. 289.

Ethyl-benzoic acids $C_2H_5.C_6H_4.CO.OH$.—The three isomerides are known. The o-acid results in the reduction of o-aceto-phenone-carboxylic acid, of methyl phthalide (B. **29,** 2533), and of phthalic acetic acid $C_6H_4\begin{cases}C=CHCO_2H\\ \quad\rangle O\\ CO\end{cases}$ with hydriodic acid (B. **10,** 2206), and in

that of the chloro-vinyl-benzoic acids with sodium amalgam (B. **27,** 2761). o- m-, and p-Ethyl-benzoic acids melt at 68°, 47°, and 112° (B. **21,** 2830 ; A. **216,** 218) respectively.

Dimethyl-benzoic acids $(CH_3)_2C_6H_3CO_2H$. — Mesitylenic acid is the most important member of this group. It is formed when mesitylene, symmetrical or [1, 3, 5]-trimethyl-benzol is oxidised with dilute nitric acid. Iso-xylol or m-xylol is obtained when this acid is distilled with lime. These reactions are the basis of the evidence that iso-xylol and its oxidation products, m-toluic acid and iso-phthalic acid, are m-di-substitution products of benzene. Further oxidation of mesitylene acid leads to *uvitinic acid* and *trimesic acid.*

1, 2-Dimethyl-3-benzoic acid, *α-hemellithic acid,* m.p. 144° (B. **19,** 2518)
1, 2-Dimethyl-4-benzoic acid, *p-xylylic acid,* . „ 163° (B. **17,** 2374)
1, 3-Dimethyl-2-benzoic acid, ... „ 98° (B. **11,** 21)
1, 3-Dimethyl-4-benzoic acid, ... „ 126° (B. **12,** 1968)
1, 3-Dimethyl-5-benzoic acid, **mesitylenic acid,** . „ 166° (A. **141,** 144)
1, 4-Dimethyl-2-benzoic acid, *iso-xylylic acid,* . „ 132°, b.p. 268° (A. **244,** 54).

Propyl-benzoic acids $C_3H_7.C_6H_4CO_2H$. — o- and p-n-Propyl and p-iso-propyl-benzoic acids are known. p-Iso-propyl-benzoic acid, or *cumic acid,* the oxidation product of the most note. Chromic acid oxidises cumic acid to *terephthalic acid,* and potassium permanganate converts it into *p-oxy-iso-propyl-benzoic acid* and *p-acetyl-benzoic acid* :

o, n-Propyl-benzoic acid . . m.p. 58° (B. **11,** 1014)
p, n-Propyl-benzoic acid . . „ 138° (B. **21,** 2231)
o-Iso-propyl-benzoic acid . „ 51° (A. **248,** 63)
Cuminic acid, p-Iso-propylb. „ 117° (A. **219,** 279 ; B. **20,** 860).

Trimethyl-benzoic acids.—Five are known. Durylic acid is obtained from durol, and α-, β-, and γ-iso-durylic acids from iso-durol (B. **27,** 3446), upon oxidation with dilute nitric acid. β-Iso-durylic acid or mesitylene-carboxylic acid can also be formed from acetyl-mesitylene (p. 268) (B. **25,** 503).

1, 2, 3-Trimethyl-4-benzoic acid, Prehnitylic acid, melts at 167°
1, 2, 3-Trimethyl-5-benzoic acid, α-Iso-durylic acid, „ 215°
1, 2, 4-Trimethyl-5-benzoic acid, Durylic acid, „ 150°
1, 2, 4-Trimethyl-6-benzoic acid, γ-Iso-durylic acid, „ 127°
1, 3, 5-Mesitylene-carboxylic acid, β-Iso-durylic acid, „ 152°.

Tetramethyl-benzoic acids.—Several are known : 1, 2, 3, 4-*tetramethyl-5-benzoic acid,* melting at 165°, is the oxidation product of pentamethyl-benzene (B. **20,** 3287) ; 1, 2, 3, 5-*tetramethyl-6-benzoic acid,* durol-carboxylic acid (B. **29,** 2569) ; 2, 3, 5, 6-*tetramethyl-benzoic acid* melts at 127° (B. **29,** R. 233).

Pentamethyl-benzoic acid $(CH_3)_5.C_6.CO_2H$, melting at 210°, is made according to method 9 (B. **22,** 1221).

Phenyl-fatty acids.—The most important representatives of this group are phenyl-acetic acid or α-toluic acid, β-phenyl-propionic acid or hydro-cinnamic acid, and α-phenyl-propionic acid or hydratropic acid. The synthesis and decomposition of the phenyl-fatty acids can be realised in the same manner as the synthesis and decompositions of the fatty acids (I. 251). The general methods of formation 2, 3, 4, 5, 6, 11, 12*b*,

13, 14, 15, and 16 are particularly prominent in the formation of the phenyl-fatty acids.

Phenyl-acetic acid, *alpha-toluic acid* $C_6H_5.CH_2.CO_2H$, melts at 76° and boils at 262°. This acid is formed from toluol just as acetic acid is obtained from methane. Toluol is converted into benzyl chloride, and this into benzyl cyanide, which is then digested with sulphuric acid (B. **19,** 1950; **20,** 592); or the benzyl chloride is converted into benzyl-magnesium chloride by magnesium in ether solution, and CO_2 is conducted through (B. **35,** 2523, 2694):

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2Cl \begin{cases} \longrightarrow C_6H_5CH_2CN \longrightarrow C_6H_5CH_2CO_2H \\ \longrightarrow C_6H_5CH_2MgCl \longrightarrow C_6H_5CH_2CO_2H \end{cases}.$$

It can also be obtained from phenyl-chloracetic acid $C_6H_5.CHCl.CO_2H$ (B. **14,** 240), from phenyl-glycollic acid or almond acid $C_6H_5CH(OH).CO_2H$, and phenyl-glyoxylic acid $C_6H_5.CO.CO_2H$, by reduction.

It is produced when phenyl-malonic acid is heated (see method 15), and it appears in the decay of albuminates (B. **12,** 649). It may be prepared, furthermore, from bromo-benzene, chloracetic ester, and copper (B. **2,** 738); by heating aceto-phenone with yellow ammonium sulphide; and by oxidising phenyl-pyro-racemic acid with H_2O_2. Chromic acid oxidises it to benzoic acid. Chlorine, with heat, converts it into phenyl-chloracetic acid, while in the cold the halogens replace the aromatic hydrogen.

Tolyl-acetic acids, alpha-xylic acids $C_6H_4\begin{matrix}CH_3\\CH_2.CO_2H\end{matrix}$.—The three isomeric acids have been obtained from the three xylene bromides. The *ortho*-acid melts at 89°, the *meta*- at 61°, and the *para*- at 91° (B. **20,** 2051; **24,** 3965).

p-Xylyl-acetic acid $(CH_3)_2[1,4]C_6H_3CH_2COOH$, m.p. 128°, from aceto-p-xylol and Am_2S (C. 1897, II. 411).

Hydro-cinnamic acid, β-phenyl-propionic acid $C_6H_5.CH_2.CH_2.CO_2H$, m.p. 47° and b.p. 280°, is isomeric with α-phenyl-propionic acid, the three alpha-xylic acids, the three ethyl-benzoic acids, and the six dimethyl-benzoic acids. It is obtained: from cinnamic acid $C_6H_5CH:CHCOOH$ by reduction, *e.g.* with electrolytic hydrogen evolved at a Hg cathode (C. 1903, II. 107), or with sodium amalgam or HI (B. **30,** 1680); from phenyl-ethyl-magnesium bromide $C_6H_5CH_2.CH_2.MgBr$ and CO_2 (C. 1904, I. 1493); from propio-phenone with yellow Am_2S; from phenyl-ethyl cyanide (A. **156,** 249); from benzyl-aceto-acetic ester (B. **10,** 758) and benzyl-malonic ester (A. **204,** 176); also from benzyl-acetic ester, with sodium (A. **198,** 300) (see, further, methods 5, 6, 14, 15, and 16); and in the decay of albuminoid substances (B. **12,** 649). Chromic acid oxidises it to benzoic acid.

The aliphatic haloid hydro-cinnamic acids, readily obtained by the addition of haloid acids and halogens to cinnamic acid, will be described after phenyl-lactic and phenyl-glyceric acids.

Hydratropic acid, α-phenyl-propionic acid $C_6H_5CH(CH_3).CO_2H$, b.p. 265°, is an oil, volatile in aqueous vapour. It results from the reduction of atropic acid or α-phenyl-acrylic acid $C_6H_5C(=CH_2).CO_2H$, and in the action of hydriodic acid upon the prussic acid addition product of aceto-phenone—the nitrile of atro-lactinic acid (A. **250,** 135).

Higher homologues of these acids are usually made according to

the following reactions :—(1) By reduction of homologous cinnamic acids (*q.v.*), which can be readily prepared by Perkins' reaction from the aromatic aldehydes. (2) By the reduction of homologous almond acids, obtained from homologous phenyl-glyoxylic acids. The latter result upon oxidising homologous acetyl-benzols with potassium permanganate. (3) From the alkyl-phenyl ketones with yellow Am_2S. (4) From alkylised benzyl cyanides, which are produced by the action of alkylogens upon sodium-benzyl cyanide. (5) By the action of benzene and aluminium chloride upon aliphatic lactones and olefin-carboxylic acids.

γ-Phenyl-butyric acid $C_6H_5.CH_2.CH_2.CH_2.COOH$, m.p. 51·7°, is formed by the reduction of phenyl-butyro-lactone or of phenyl-crotonic acid (C. 1899, I. 792) from ω-bromo-propyl-benzol, Mg, and CO_2 (B. **48,** 1233); also from phenyl-propyl ketone with Am_2S (*J. pr. Ch.* 2, **80,** 197).

β-Phenyl-butyric acid $C_6H_5(CH_3)CH.CH_2.COOH$, m.p. 39°, is formed (1) by reduction of β-methyl-cinnamic acid (B. **40,** 1595); (2) from crotonic acid, benzene, and Al_2Cl_6 (C. 1908, II. 1023); (3) from phenyl-iso-propyl ketone with Am_2S; (4) by the disintegration of the addition product of CH_3MgI and benzal-malonic ester (C. 1905, II. 1023).

α-Phenyl-iso-butyric acid $C_6H_5C(CH_3)_2COOH$, m.p. 78°, b.p.$_{10}$ 150°–155°, from benzene, Al bromide, and **α-bromiso-butyric acid** (C. 1899, II. 1047).

β-Phenyl-iso-butyric acid, benzyl-methyl-acetic acid $C_6H_5CH_2CH(CH_3)COOH$, m.p. 37°, b.p. 272°, is split up by means of its quinine salt into optically active components (C. 1902, I. 661).

δ-Phenyl-valerianic acid $C_6H_5(CH_2)_4COOH$, m.p. 59°, by reduction of phenyl-cumalin with HI (B. **29,** 1675, R. 14).

α-Phenyl-iso-valerianic acid $(CH_3)_2CH.CH(C_6H_5)COOH$, m.p. 59°, and **α-methyl-β-phenyl-butyric acid** $CH_3CH(C_6H_5)CH(CH_3)COOH$, m.p. 132°, from iso-propylidene-acetic acid and tiglinic acid with benzene and Al_2Cl_6 (C. 1908, II. 1100). **α-Methyl-γ-phenyl-butyric acid** $C_6H_5CH_2CH_2CH(CH_3)COOH$, m.p. 67°, from phenyl-iso-butyl ketone and Am_2S (*J. pr. Ch.* 2, **80,** 198).

(*b*) Derivatives of the Aromatic Monocarboxylic Acids.

The derivatives of benzoic acid and its homologues arrange themselves into two groups. The first group comprises those compounds resulting from the alteration of the carboxylic group (see Acetic acid, Vol. I.), and the second group the aromatic substitution products with the exception of the phenol monocarboxylic acids. The first group divides itself into A, the benzoyl-compounds; B, the benzenyl compounds and the derivatives of ortho-benzoic acid. The chemistry of no single carboxylic acid has been so fully developed as that of benzoic acid.

Benzoyl Compounds.

1. Esters of the Monobasic Aromatic Acids (Vol. I.).—The benzoic esters of the alcohols and phenols can be prepared like the acetic esters. Like the latter, they are frequently employed in determining the number of alcoholic hydroxyl groups present in a compound. They are formed (1) by the action of hydrochloric acid upon an alcoholic solution

of benzoic acid. In the substituted benzoic acids the following rule is found :—Ortho-substituted acids take a longer time to esterify than m- and p-substituted acids (*Z. physik. Ch.* **24,** 221). In the diortho-substituted acids, like mesitylene-carboxylic acid, 2, 6-dibromo-, 2, 4, 6-tribromo-, and 2, 4, 6-trinitro-benzoic acid, the ester formation is usually so slow on boiling with alcohol and HCl that it is practically non-existent (B. **28,** 1468 ; **29,** 1399, 2301 ; **33,** 2026 ; **42,** 317 ; C. 1901, II. 1117). But the ester formation is easily accomplished by heating these acids to 180°–200° with alcohol, even without a catalyser (*Z. physik. Ch.* **66,** 275). The esters of these acids are also obtained readily (2) from the silver salts with halogen alkyls, or the alkali salts with dimethyl sulphate ; (3) by treating with diazo-methane (B. **31,** 501). Furthermore, the esters of benzoic acid are produced (4) by the action of benzoyl chloride or benzoic anhydride upon alcohols, alcoholates, phenols, and phenolates. In carrying out the second reaction it is advisable gradually to add sodium hydroxide, and shake the alkaline, aqueous solution of the alcohols with benzoyl chloride until there is a permanent alkaline reaction (Baumann, B. **19,** 3218). In this manner, also, the benzoyl ethers of the poly-alcohols, the polyoxy-aldehydes—*e.g.* of the glucoses—have been obtained, and nearly all have been completely benzoylated (B. **22,** R. 668).

Methyl-benzoic ester boils at 199°. The **ethyl ester** boils at 213° ; the **n-propyl ester** at 229° ; the **n-butyl ester** at 247°. **Glycol dibenzoate** melts at 73° (B. **23,** 2498). **Glycerol tribenzoate** melts at 76° (B. **24,** 779 ; C. 1902, I. 1224). **Erythrol tetrabenzoate** melts at 187°. **Mannitol hexabenzoate** melts at 124°. **Glucose pentabenzoate** melts at 179°.

Methylene dibenzoate $CH_2(OCOC_6H_5)$, m.p. 96°, by heating benzoyl chloride with trioxy-methylene and zinc chloride, an intermediate product being $Cl.CH_2OCOC_6H_5$ (C. 1901, II. 396, 682).

Benzoyl-glycollic acid $C_6H_5CO.OCH_2.CO_2H$ consists of large prisms. It results when nitrous acid acts upon hippuric acid. **Phenyl-benzoic ester** melts at 71° and boils at 314° (A. **210,** 255 ; B. **24,** 3685). The **benzyl ester** melts at 20° and boils at 323° (B. **20,** 647). It occurs in Peru balsam (A. **152,** 130). For the benzoyl compounds of the homologous phenols, see Phenols.

o-, m- and **p-Toluic methyl esters,** b.p. 213° and 221°, m.p. 34° (C. 1901, II. 290).

Phenyl-acetic ethyl ester $C_6H_5CH_2COOC_2H_5$, b.p. 226°, from benzyl cyanide, alcohol, and HCl (A. **296,** 361). Phenyl ester, m.p. 38°, b.p.$_{15}$ 180°. Phenyl-acetic ester adds itself to $\alpha\beta$-unsaturated ketones and acid esters (B. **42,** 4496) With ethyl nitrate and potassium ethylate it gives **phenyl-nitro-acetic ester** $C_6H_5CH(NO_2)COOR$, which easily eliminates the carbox-ethyl group and forms phenyl-nitro-methane. With ethyl nitrite and K ethylate, iso-nitro-phenyl-acetic ester is formed (B. **42,** 1930). **β-Phenyl-propionic ethyl ester,** b.p. 248°.

2. AROMATIC ACID HALOIDS OR HALOID ANHYDRIDES OF THE AROMATIC ACIDS.—The methods pursued in the preparation of these bodies are similar to those employed for the corresponding fatty derivatives.

Benzoyl chloride $C_6H_5.COCl$, melting at −1° and boiling at 198°, is isomeric with the chlorinated benzaldehydes $Cl.C_6H_4.CHO$. It is a liquid with penetrating odour. It is formed from benzoic acid, phos-

phorus pentoxide, and hydrochloric acid (B. **2,** 80); from benzaldehyde and chlorine; from sodium benzoate and phosphorus oxy-chloride; and from benzoic acid and phosphorus pentachloride. The action of phosgene and aluminium chloride or oxalyl chloride (B. **41,** 3566) upon benzene hydrocarbons, and of anhydrous oxalic acid upon benzo-trichloride (A. **226,** 20), are only applicable in the preparation of the chlorides of benzene-carboxylic acids.

With antimony chloride, benzoic acid combines to form $C_6H_5COOH.SbCl_5$, m.p. 71°, which, on heating, yields benzoyl chloride (B. **35,** 1117).

The history of benzoyl chloride, the first-discovered chloride of a carboxylic acid, was given in connection with the fatty acid chlorides (I. 257). Benzoyl chloride is readily accessible and very reactive; it is therefore one of the most frequently used compounds in various reactions.

o-, m-, and **p-Toluyl chlorides** boil at 212°, 220°, and 95° (10 mm.) respectively. **Phenyl-acetyl chloride** $C_6H_5.CH_2COCl$ boils at 102° (17 mm.) (B. **20,** 1389).

Benzoyl bromide $C_6H_5.COBr$, melting about 0° and boiling at 218°, results from the action of phosphorus tribromide upon benzoic acid (B. **14,** 2473). **Benzoyl iodide,** consisting of crystalline flakes, is produced when potassium iodide or magnesium iodide acts upon benzoyl chloride (B. **8,** 266; C. 1909, II. 1132). **Benzoyl fluoride,** from benzoyl chloride and AgF, boils at 145°.

So far as concerns properties, **benzoyl azimide** or **benzoyl nitride,** to be treated later in connection with benzoyl-hydrazin, attaches itself to the halogen anhydrides of benzoic acid.

The acid chlorides and haloid anhydrides connect the mixed anhydrides of aromatic acids with inorganic acids.

Benzoyl nitrate $C_6H_5COONO_2$, a light yellow oil, is formed by the transformation of benzoyl chloride with silver nitrate at low temperatures. On heating, it decomposes into nitric oxides and benzoic anhydride. Water decomposes it into benzoic and nitric acids. It nitrifies aromatic substances (B. **39,** 3798).

Benzoyl nitrite C_6H_5COONO, an unstable oil, from silver benzoate and nitrosyl-chloride (C. 1904, II. 511).

Benzoic-boric anhydride $(C_6H_5COO)_3B$, m.p. 145°, by heating benzoic acid with aceto-boric anhydride (B. **36,** 2224).

Benzoic-arsenic anhydride $(C_6H_5COO)_3As$, m.p. 155°, on melting benzoic acid with aceto-arsenic anhydride (C. 1906, I. 21).

3. ACID ANHYDRIDES (I. 259).—**Benzoic anhydride** $(C_6H_5.CO)_2O$, melting at 42° and boiling at 360°, is obtained from benzoyl chloride and sodium benzoate or silver benzoate; from benzoyl chloride and benzo-trichloride upon digesting them with anhydrous oxalic acid; from benzoyl chloride by means of lead nitrate (B. **17,** 1282) or sodium nitrite (B. **24,** R. 371); and by the action of concentrated sulphuric acid upon benzo-trichloride (B. **12,** 1495).

Mixed anhydrides are obtained from benzoic acid treated with anhydrides of acid chlorides, pyridin or quinolin (C. 1901, I. 347; B. **42,** 3483). **Aceto-benzoic anhydride** $C_6H_5.COOCOCH_3$, m.p. 10°, b.p.$_{17}$ 125°–140°, decomposes, on heating, into acetic acid and benzoic acid.

Benzoic-carbonic anhydride $(C_6H_5COO)_2CO$, an oil, from benzoic acid, $COCl_2$, and pyridin, yields CO_2 even at ordinary temperatures.

o- and **p-Toluic anhydride,** m.p. 37° and 95°. **Phenyl-acetic anhydride** $(C_6H_5CH_2CO)_2O$, m.p. 72° (B. **20,** 1391).

4. ACID PEROXIDES.—**Benzoyl peroxide** $(C_6H_5CO)_2O_2$, melts at 103° and deflagrates when heated. It is formed from benzoyl chloride and barium peroxide, or from benzoyl chloride, hydrogen peroxide, and sodium hydrate (B. **27,** 1511; **29,** 1727; **30,** 2003; **33,** 1043). On treating an ether solution of benzoyl peroxide with sodium alcoholate, benzoic ester is produced, together with **benzoyl-sodium-hydrogen peroxide:**

$$(C_6H_5CO)_2O_2 \xrightarrow{NaOC_2H_5} C_6H_5COOC_2H_5 + C_6H_5COOONa;$$

from the latter, even carbonic acid liberates.

Benzoyl-hydrogen peroxide C_6H_5COOOH, m.p. 41°–43°. It closely resembles hydrogen peroxide. A mixture of benzoyl-hydrogen peroxide and benzaldehyde gives first two molecules benzoic acid. Probably it is also formed in the first phase during the auto-oxidation of benzaldehyde in air; a mixture of benzaldehyde and acetic anhydride forms, under the influence of atmospheric oxygen, **benzoyl-acetyl peroxide** $C_6H_5COOOCOCH_3$, m.p. 38°, by acetylation of the benzoyl-hydrogen peroxide first formed (B. **33,** 1569; C. 1902, I. 930).

5. THIO-ACIDS AND BITHIO-ACIDS.—**Thio-benzoic acid** C_6H_5COSH, m.p. 24°, is formed by the interaction of benzoyl chloride and alcoholic potassium sulphide; also, besides triphenyl carbinol, from phenyl-magnesium bromide with COS (B. **36,** 1010). **Thio-p-toluic acid** $CH_3C_6H_4COSH$, m.p. 44°.

Benzoyl sulphide, *thio-benzoic sulphanhydride* $(C_6H_5CO)_2S$, m.p. 48°, from two molecules benzoyl chloride with one molecule sodium sulphide (B. **40,** 2862). **Benzoyl disulphide** $(C_6H_5CO)_2S_2$, m.p. 130°, from thio-benzoic acid on oxidation in ether solution by atmospheric oxygen (A. **115,** 27), or from its salts on oxidation by potassium ferricyanide (B. **40,** 2862). Thio-benzamide and thio-anilide, see below.

Dithio-benzoic acid, *phenyl-carbo-thio-acid* C_6H_5CSSH, a heavy purple oil, rather unstable, obtained from benzo-trichloride with alcoholic potassium sulphide (A. **140,** 240); from phenyl-magnesium bromide and CS_2 (B. **39,** 3219); as well as by the action of hydrogen persulphide and zinc chloride upon benzaldehyde (C. 1909, II. 1780). Methyl ester, b.p. 155°; ethyl ester, b.p. 167°; luminous red oils. The lead salt consists of purple flakes, melting at 204·5°. The alkali-salt solution gives, by oxidation with iodine, **thio-benzoyl disulphide** $(C_6H_5CS)_2S_2$, m.p. 117°, dark-red needles. **Dithio-phenyl-acetic acid** $C_6H_5CH_2CSSH$, a reddish-yellow oil, from benzyl-magnesium chloride with CS_2. Lead salt, m.p. 149°, yellow needles.

Phenyl-thio-acetyl disulphide $(C_6H_5CH_2.CS)_2S_2$, m.p. 78° (B. **39,** 3227).

Phenyl-p-tolyl-keto-sulphone $C_6H_5CO.SO_2C_6H_4CH_3$, from benzoyl chloride and sodium-toluol sulphinate, forms a hydrate of m.p. 80° (C. 1899, II. 719).

6. ACID AMIDES.—The methods of formation and the behaviour of the acid amides have been sufficiently considered in connection with the fatty acid amides. Attention was also called to the fact that the

amides of the carboxylic acids could have two constitution formulæ. Thus, benzamide has two formulæ :

I. $C_6H_5C\langle^{NH_2}_{O}$ and II. $C_6H_5C\langle^{NH}_{OH}$.

The imido-ethers are derived from the second formula (see Silver benzamide). To the methods mentioned under the amides of the fatty acids must be added, in connection with the amides of the benzol-carboxylic acids, their formation through the action of aluminium chloride upon aromatic hydrocarbons and urea chlorides.

Benzamide $C_6H_5.CO.NH_2$, melting at 130° and boiling at 288°, results (1) when benzoyl chloride is acted upon by gaseous or aqueous ammonia, or by ammonium carbonate (see Tribenzamide) ; (2) from benzoic ester and ammonia ; (3) by heating benzoic acid and ammonium thio-cyanate to 170° (A. **244**, 50) ; (4) by saponification of benzonitrile with an appropriate amount of alcoholic potash (C. 1900, I. 257) ; (5) from urea chloride, benzene, and $AlCl_3$ (A. **244**, 50). It crystallises in pearly flakes, melts at 130°, and boils near 288°. It is readily soluble in hot water, alcohol, and ether.

Sodium benzamide $C_6H_5CONHNa$ or $C_6H_5C(:NH)ONa$ results from the action of metallic sodium upon benzamide dissolved in benzene (B. **28**, 3038). On heating with acid esters it forms mixed diacylimides (B. **28**, 3038 ; C. 1900, II. 190 ; 1903, I. 157).

Silver benzamide $C_6H_5.CO.NHAg$ or $C_6H_5.C(:NH).O.Ag$, obtained by precipitating the aqueous solution of benzamide and silver nitrate with a calculated amount of sodium hydroxide, is a white crystalline powder. When digested with ethyl iodide it yields benzimido-ethyl ether (B. **28**, 1550).

Dibenzamide $(C_6H_5CO)_2NH$, melting at 148°, is obtained from benzonitrile with fuming sulphuric acid, or from benzoyl chloride and benzonitrile with aluminium chloride. When distilled under a pressure of 15 mm. dibenzamide breaks down into benzo-nitrile and benzoic acid (B. **21**, 2389). **Sodium dibenzamide** $(C_6H_5CO)_2NNa$ is a shining white powder. It is formed when sodium acts upon dibenzamide dissolved in xylol.

Tribenzamide $(C_6H_5CO)_3N$, melting at 202°, results in the action of benzoyl chloride in ethereal solution upon sodium dibenzamide, and together with benzamide and dibenzamide when benzoyl chloride acts upon ammonium carbonate (B. **25**, 3120).

Benzoyl-chlorimide $C_6H_5CONHCl$ melts at 113°. **Benzoyl-bromimide** $C_6H_5.CONHBr$ melts with decomposition at 170°. **Dibenzamide chloride** $(C_6H_5CO_2)_2NCl$, m.p. 89° (C. 1902, II. 359). **Methyl-** and **dimethyl-benzamide** $C_6H_5CON(CH_3)_2$ melt at 78° and 41°.

N-methylol-benzamide $C_6H_5CO.NH.CH_2OH$, m.p. 106°, from benzamide and formaldehyde, under the influence of alkaline condensing agents. On heating alone, or in aqueous solution, it easily dissolves into its components. Chromic acid oxidises it to **formyl-benzamide** $C_6H_5CONHCHO$, m.p. 120°. With phenyl-hydrazin the latter gives 2, 5-diphenyl-triazol (*q.v*) (A. **343**, 223). **Benzoyl-benzylamine** $C_6H_5CO.NH.CH_2C_6H_5$, m.p. 105° (B. **26**, 2273).

We get **benzanilide** $C_6H_5.CO.NH.C_6H_5$, **phenyl-benzamide**, on mixing aniline and benzoyl chloride. It can also be made by the action of

aluminium chloride upon benzene and carbanile, and upon heating benzo-phenoxime $(C_6H_5)_2C:N.OH$ with concentrated sulphuric acid, acetyl chloride, or glacial acetic acid containing hydrochloric acid, to 100°, or with glacial acetic acid alone to 180° (B. **20,** 2581). **Sodium benzanilide,** see C. 1900, II. 190.

When benzanilide is boiled with sulphur it becomes *benzenyl-amido-thio-phenol* or μ-phenyl-benzo-thiazole. *o-*, *m-*, and *p-Benzoyl-toluides* $C_6H_5CONH.C_6H_4CH_3$ melt at 131°, 125°, and 158°.

Diphenyl-benzamide $C_6H_5CO.N(C_6H_5)_2$, m.p. 177°, results from diphenyl-amine and benzoyl chloride, as well as from diphenyl-urea chloride: (1) by condensation with benzene and aluminium chloride (B. **20,** 2119); (2) by heating with benzoic acid in pyridin solution (B. **41,** 636).

Methylene-dibenzamide, *hipparaffin* $CH_2(NH.CO.C_6H_5)_2$, m.p. 221°, is obtained in the oxidation of hippuric acid with PbO_2 and dilute sulphuric or dilute nitric acid, and results from formaldehyde, benzonitrile, and hydrochloric acid (B. **25,** 311); or from boiling benzamide with formaldehyde and dilute sulphuric acid (A. **343,** 226).

Ethylidene-dibenzamide $CH_3.CH(NHCOC_6H_5)_2$, m.p. 204° (B. **7,** 159).

Ethylene-dibenzamide $C_6H_5CO.NH.CH_2.CH_2.NH.CO.C_6H_5$, m.p. 249°, when heated alone, or with hydrochloric acid, yields ethylene-benzenyl-amidine, benzoic acid splitting off at the same time (B. **21,** 2334).

Benzoyl-iso-cyanate, *carbonyl-benzamide* $C_6H_5CON:CO$, m.p. 26°, b.p.$_{10}$ 88°, from silver cyanate and benzoyl chloride, yields dibenzoyl-urea in water, and **benzoyl-urethane** $C_6H_5CONH.CO_2C_2H_5$, m.p. 111°, in alcohol (B. **36,** 3218).

Hippuric acid, *benzoyl-glycocoll* $CH_2\langle^{NH.CO.C_6H_5}_{CO_2H}$, m.p. 187°, decomposes at 240° into benzoic acid, benzo-nitrile, and prussic acid. It occurs in considerable amount in the urine of herbivorous animals, in that of the cow and horse (ἵππος, horse, and οὖρον, urine), and in minute quantities in that of man. Benzoic acid, cinnamic acid, toluol, and other aromatic substances, when taken internally, are eliminated as hippuric acid. It can be obtained artificially (1) by heating benzamide with monochloracetic acid; (2) by the action of benzoyl chloride or silver glyco-collide (B. **15,** 2740); or (3) by adding sodium hydroxide to glycocoll, and shaking with benzoyl chloride (B. **19,** R. 307); and (4) by heating benzoic anhydride with glycocoll (B. **17,** 1662).

History.—Liebig, in 1829, recognised that hippuric acid was a different body from benzoic acid, and, to indicate its origin, named it hippuric acid. In 1839 he established its constitution. Dessaignes (1846) showed that, upon boiling with strong alkalies or acids, it was resolved into glycocoll and benzoic acid (*J. pr. Ch.* 1, **37,** 244). In 1848 Strecker converted the acid by means of nitrous acid into benzoyl-glycollic acid (A. **68,** 54), and in 1853 Dessaignes synthesised hippuric acid from benzoyl chloride and zinc glyco-collide (A. **87,** 325).

Hippuric acid crystallises in rhombic prisms, and dissolves in 600 parts cold, and readily in hot water, and alcohol. Boiling acids, or alkalies, decompose hippuric acid into benzoic acid and glycocoll.

Compare *hipparaffin* (above), *benzoyl-glycollic acid,* for other trans-

formations of hippuric acid. Hippuric acid condenses with benzaldehyde, sodium acetate, and acetic anhydride to benzoyl-amido-cinnamic anhydride $C_6H_5CH:C\langle^{N=CC_6H_5}_{CO-O}$ (A. **337**, 265).

Silver salt $C_9H_8AgNO_3$. The **ethyl ester** melts at 60° (*J. pr. Ch.* 2, **15**, 247). It is converted by PCl_5 into **hippuro-flavin** $C_{18}H_{10}O_4N_2$, consisting of citron-yellow crystals (B. **21**, 3321; **26**, 2324; A. **312**, 81). Benzaldehyde and sodium acetate change it to **benzoyl-amido-cinnamic ester** (A. **275**, 12). The **phenyl ester** melts at 104°. When boiled with $POCl_3$ it passes into **anhydro-hippuric phenyl ester**, melting at 42° (B. **26**, 2641).

With formic acid ester and sodium ethylate, hippuric ethyl ester condenses to **formyl-hippuric ester** $C_6H_5CO.NH.CH(CHO)CO_2C_2H_5$, which is reduced by sodium amalgam to **benzoyl-serinic ester** $C_6H_5CO.NH.CH(CH_2OH)CO_2C_2H_5$, m.p. 80°. The latter is split up by H_2SO_4 into benzoic acid and *i-serin*; with P_2S_5 it passes into **benzoyl-cystein ester** $C_6H_5CONH.CH(CS_2SH)CO_2C_2H_5$, m.p. 185°, from which, by saponification with concentrated HCl, we obtain *i-cystein*, or its oxidation product, *i-cystin* (cp. Vol. I., and A. **337**, 236).

Hippuric acid nitrile $C_6H_5CONHCH_2CN$, m.p. 144°, from amido-aceto-nitrile, benzoyl chloride, and NaHO (B. **36**, 1646). **Hippuryl-hydrazin** $C_6H_5CO.NHCH_2CO.NH.NH_2$, m.p. 162°, from hippuric ethyl ester and hydrazin; cp. hippuryl-phenyl-buzylene and hippurazide (B. **29**, R. 181).

Benzoyl-alanin $C_6H_5CONH.CH(CH_3)COOH$, m.p. 166°, and **benzoyl-α-amido-iso-butyric acid** $C_6H_5CONHC(CH_3)_2COOH$, m.p. 198°, on heating with acetic anhydride, readily pass into anhydrides resembling lactone: **benzoyl-alanin anhydride** $C_6H_5C=N-\underset{O-CO}{}\rangle CH(CH_3)$, m.p. 39°, and **benzoyl-α-amido-iso-butyric anhydride** $C_6H_5C=N-\underset{O-CO}{}\rangle C(CH_3)_2$, m.p. 34° (cp. the similarly constituted acyl-anthranilic acids). Ammonia, aniline, and HCl burst the lactone ring, with formation of the amides, anilides, and chlorides of the corresponding benzoyl-amido-acids. With α-amido-acids they similarly combine to form benzoylated dipeptides, *e.g.* **benzoyl-alanyl-glycocoll** $C_6H_5CONH.CH(CH_3)CONHCH_2COOH$, **Benzoyl-alanyl-alanin** $C_6H_5CONH.CH(CH_3)CONH.CH(CH_3)COOH$, etc. (*J. pr. Ch.* 2, **81**, 49, 473)

Benzoyl-asparaginic acid, see B. **43**, 661.

7. Acid Hydrazides. — **Benzoyl-hydrazin** $C_6H_5CONHNH_2$, m.p. 112°, from benzoic ester and hydrazin hydrate, or by heating hydrazin benzoate (B. **35**, 3240); in alkaline solution benzoyl-hydrazin suffers an auto-reduction, leading to benzal-benzoyl-hydrazin $C_6H_5CONHN:CHC_6H_5$, and subsequently benzalazin (B. **33**, 2561). With excess of benzoic ester hydrazin forms **dibenzoyl-hydrazin** $(C_6H_5CO.NH)_2$, m.p. 238°, also generated by the action of benzoyl chloride upon alkaline hydrazin solutions (C. 1899, I. 1240). On boiling with alcoholic potash, it yields a potassium salt $(C_6H_5CO)_2N_2HK$; the corresponding silver salt with iodine gives **azo-dibenzoyl** $(C_6H_5CO)_2N_2$, m.p. 118° (B. **33**, 1769). **Tri-** and **tetrabenzoyl-hydrazin**, m.p. 206° and 238°, are obtained by further benzoylation of dibenzoyl-hydrazin (C. 1904, II. 97).

Sym. benzoyl-phenyl-hydrazin, m.p. 168° (B. **19**, 1203), on oxidation

with mercuric oxide or nitrous acid is converted into **benzoyl-azo-benzol** $C_6H_5CON_2C_6H_5$, red prisms, melting at 80° (C. 1909, II. 84) ; the latter gives with HCl an addition product which changes into **o-chloro-phenyl-benzoyl-hydrazin** (B. **30,** 319) :

$$C_6H_5CONH.NClC_6H_5 \longrightarrow C_6H_5CONHNH[1]C_6H_4[2]Cl.$$

Unsym. benzoyl-phenyl-hydrazin, m.p. 70° (B. **26,** 945, R. 816).

Dibenzoyl-phenyl-hydrazin $C_6H_5.CO.N(C_6H_5).NHCOC_6H_5$, m.p. 177°.

Benzal-benzoyl-hydrazin $C_6H_5CO.NHN.CHC_6H_4$, m.p. 203°, from benzoyl-hydrazin and benzaldehyde, or from benzalazin with benzoyl chloride (C. 1900, I. 334). The corresponding silver salt $C_6H_5CONAgN$: CHC_6H_5 passes with iodine into *diphenyl-furo-diazol* $C_6H_5C\overset{N.N}{\underset{O}{<}}CC_6H_5$, and with benzoyl chloride into *diphenyl-benzoyl-dihydro-furo-diazol* $C_6H_5C\overset{N—N.COC_6H_5}{\underset{O—CH.C_6H_5}{<}}$ (*J. pr. Ch.* 2, **70,** 393).

Phenyl-acetic hydrazide, m.p. 116°.

Hydro-cinnamic hydrazide, m.p. 103°.

8. ACIDYL-AZIDES. — **Benzoyl-azide,** *benzoyl nitride, azimide,* $C_6H_5CON\overset{N}{\underset{N}{<\!\!\|}}$, m.p. 20°, is formed when sodium nitrite, and acetic acid, act upon benzoyl-hydrazin (B. **23,** 3023). Its odour is intensely like that of benzoyl chloride ; it volatilises in part with aqueous vapour without decomposition, and explodes with slight detonation upon the application of heat. It is insoluble in water, very soluble in ether, and rather readily soluble in alcohol. It gives a neutral reaction. It breaks down, on boiling with alkalies, into benzoic acid and potassium azo-imide (B. **23,** 3029). On heating in benzene solution it is clearly divided up into N_2 and **phenyl iso-cyanate:**

$$C_6H_5CON\overset{N}{\underset{N}{<\!\!\|}} \longrightarrow [C_6H_5CON<] \longrightarrow C_6H_5N:C:O$$

(B. **42,** 2339).

Heating with alcohol and water leads to the evolution of N_2, and the formation of the transformation products of phenyl iso-cyanate : phenyl-urethane $C_6H_5NH.CO.OC_2H_5$, and carbanilide $CO(NHC_6H_5)_2$. Boiling with acid hydrazides yields **acidylated semi-carbazides** (B. **29,** R. 981) :

$$C_6H_5CON_3+C_6H_5CONHNH_2 = N_2+C_6H_5NHCONHNHCOC_6H_5$$

and **p-bromo-benzazide,** m.p. 46° (*J. pr. Ch.* 2, **58,** 190). **Phenyl-acetic azide** $C_6H_5CH_2CON_3$ and **hydro-cinnamic azide** $C_6H_5CH_2CH_2CON_3$ with alcohol yield the urethanes of benzyl-amine and phenyl-ethyl-amine (*J. pr. Ch.* 2, **64,** 297). The azides can also be obtained by the action of salts of diazo-benzol upon the acid hydrazides.

Hippurazide $C_6H_5CO.NH.CH_2.CO.N_3$, m.p. 98°, results when sodium nitrite and acetic acid act upon hippuryl-hydrazin. It is decomposed by mineral acids, alkalies, ammonia, and amines, with the elimination of *hydrazoic acid.* When boiled with alcohols, and with water, N_2 is evolved, and there result **hippenyl-urethane** $C_6H_5CONHCH_2NHCOOR$ and **dihippenyl-urea** $(C_6H_5CONHCH_2NH)_2CO$ (B. **29,** R. 183).

The action of hippurazide upon glycocoll, glycyl-glycin, alanin, etc. (Vol. I.), gives the benzoyl derivatives of di- and poly-peptides, like $C_6H_5CONHCH_2CONHCH_2COOH$, $C_6H_5CONHCH_2CONHCH_2CO.NHCH_2COOH$, $C_6H_5CONHCH_2CONHCH_2CONHCH_2CONHCH_2COOH$ (*J. pr. Ch.* 2, **70**, 57).

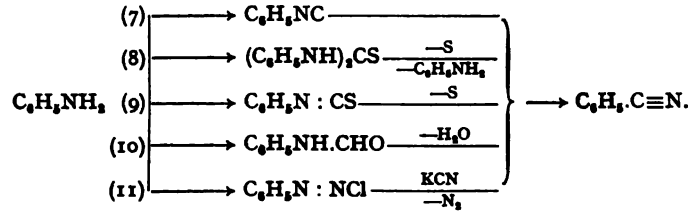
9. NITRILES OF THE AROMATIC MONOCARBOXYLIC ACIDS.—The aromatic nitriles are connected by numerous reactions with the principal classes of the aromatic derivatives. They are produced, like the nitriles of the fatty acids, (1) from the corresponding ammonium salts; (2) from the corresponding acid amides, by the withdrawal of water with P_2O_5, PCl_5, and $SOCl_2$ (B. **26**, R. 401); (3) by action of bromine, and caustic alkali, upon the primary phenyl-alkyl-amines; (4) from the aldoximes by the action of acetyl chloride or acetic anhydride. There is also (5) the method of distilling aromatic monocarboxylic acids, with potassium sulpho-cyanide, or, better, with lead sulpho-cyanide (B. **17**, 1766):

$$2C_6H_5CO_2H+(CNS)_2Pb = 2C_6H_5CN+2CO_2+PbS+H_2S.$$

Nuclear-synthetic Methods.—(6) The direct replacement of the halogens in the benzol hydrocarbons by the cyanogen group is of exceptional occurrence—*e.g.* when chloro- and bromo-benzol are conducted over strongly ignited potassium ferrocyanide, or when benzol iodide is heated to 300° with silver cyanide, the product being cyano-benzol.

However, the phenyl-carbinol chlorides—*e.g.* $C_6H_5CH_2Cl$—are as readily transposed, as the alkylogens, into nitriles of the phenyl-fatty acids by means of potassium cyanide.

The nitriles are also intimately related to the anilines, sulphonic acids, and phenols. Thus, aniline yields (7) phenyl-carbylamine, which, upon the application of heat, is rearranged into the isomeric nitrile. They are also produced (8) on heating the diphenyl-thio-ureas with zinc dust; (9) by desulphurising the phenyl-mustard oils with copper; (10) by distilling the formanilides with concentrated hydrochloric acid or with zinc dust (B. **17**, 73); (11) by decomposing diazobenzene chloride with potassium cyanide and copper sulphate.



(12) By distilling the alkali-benzene sulphonates with potassium cyanide or yellow prussiate of potash; (13) the distillation of the triphenyl phosphates with potassium cyanide or ferrocyanide; (14) alkyl benzyl-cyanides are formed by the interaction of sodium-benzyl cyanide and alkylogens, $C_6H_5.CHNa.CN+C_2H_5I = C_6H_5CH(C_2H_5)CN$; (15) the hydrogen atoms of the benzols are directly replaced by the cyanogen group, (*a*) if cyanogen gas be conducted into the boiling hydrocarbon

mixed with aluminium chloride (B. **29,** R. 185); (*b*) in the action of mercury fulminate C : NOHg upon benzene and anhydrous ACl_3, benzo-nitrile (80 per cent.) is formed, while hydrated $AlCl_3$ leads to the formation of benzaldoxime (B. **36,** 10). On the action of chlorine and bromine cyanide upon benzene hydrocarbons in the presence of Al chloride, see B. **33,** 1052.

Properties and Behaviour.—The benzo-nitriles are indifferent, agreeably smelling liquids, or solids with low melting-points. Their reactions are very numerous, but it may be mentioned that boiling alkalies or acids convert them into the corresponding aromatic acids, while nascent hydrogen, best from alcohol and sodium, changes them to primary amines. They yield *amide iodides* with hydriodic acid.

They combine with alcohols and HCl to form imido-ethers, with anilines to *amidines*, and with hydroxylamine to *amidoximes*.

Benzo-nitrile, *cyano-benzol* $C_6H_5.CN$, boiling at 191°, with sp. gr. 1·023 (0°), is isomeric with phenyl-carbylamine, and is best obtained from benzene-sulphonic acid by method 12, or from benzoic acid by method 5. It is an oil with an odour resembling that of oil of bitter almonds.

When it is dissolved in fuming sulphuric acid, or boiled with sodium, or acted upon by other condensing agents, benzo-nitrile polymerises to *cyano-phenin* $C_3N_3(C_6H_5)_3$. Upon nitration the product is almost exclusively m-nitro-benzo-nitrile. For other transpositions, see Benzo-imido-ethers and Thio-benzamide.

Alphyl-cyanides: o-, m-, and **p-Tolu-nitriles,** *cyano-toluols* $CH_3.C_6H_4CN$ boil at 203°, 213°, and 218°. The p-body melts at 29°. **p-Xylo-nitrile** boils at 231° (B. **18,** 1712). **1, 3-Xylo-4-nitrile** melts at 24° and boils at 222° (B. **21,** 3082). **Cumo-nitrile** $(CH_3)_2.CH[4]C_6H_4[1]CN$ boils at 244°.

Nitriles of Phenyl-fatty Acids.—Benzyl cyanide, *phenyl-aceto-nitrile* $C_6H_5.CH_2CN$, b.p. 232°, with specific gravity 1·014 (18°), is isomeric with the three tolu-nitriles. It occurs in the ethereal oil of several cresses (*Tropæolum majus* and *Lepidium sativum*) (B. **7,** 1293; **32,** 2335). It is artificially prepared from benzyl chloride with potassium cyanide. It yields toluic acid by saponification; by reduction β-phenyl-ethyl-amine is the product, and upon nitration it is chiefly p-nitro-benzyl cyanide which results.

As in aceto-acetic ester and malonic ester, the hydrogen of the CH_2 group, combined with the negative groups C_6H_5 and CN, is very readily replaced. Thus, sodium ethylate produces the monosodium derivative, which may be transposed by alkylogens to alkyl-benzyl cyanides (see method 14) (B. **21,** 1291, R. 197; **22,** 1238; **23,** 2070). Nitrous acid, acting upon a sodium ethylate solution of benzyl cyanide, produces iso-nitroso-benzyl cyanide (see Phenyl-glyoxalic acid). Sodium ethylate, acting upon benzyl cyanide and benzaldehyde, produces **α-phenyl-cinnamic nitrile** $C_6H_5.C(CN) : CH.C_6H_5$ (B. **22,** R. 199). It adds itself to α, β-unsaturated esters and ketones like Na-malonic ester.

Methyl-benzyl cyanides, *tolyl-aceto-nitriles* $CH_3.C_6H_4.CH_2.CN$. The o-body boils at 244°, the m-body at 241°, while the p-compound melts at 18° and boils at 243° (B. **18,** 1281; **21,** 1331).

β-Phenyl-propio-nitrile, *hydro-cinnamic nitrile* $C_6H_5CH_2CH_2CN$,

b.p. 261° (corr.) occurs in the ethereal oil of spring-cress, *Nasturtium officinale* (B. **7**, 520 ; **26**, 1971).

α-Phenyl-propio-nitrile, *hydratropic nitrile* $C_6H_5CH(CH_3)CN$, b.p. 231° (A. **250**, 123, 137).

In addition to the benzo-nitriles, the classes of bodies 10 to 31 arrange themselves with the benzenyl compounds.

10. *Amido-haloids.* 11. *Imido-chlorides.* 12. *Phenyl-hydrazide Imido-chlorides.*

Benzamide chloride $C_6H_5CCl_2NH_2$ (?) results when hydrochloric acid gas is conducted into an ether solution of benzo-nitrile (B. **10**, 1891) ; it is probably the first product resulting from the action of PCl_5 upon benzamide, which, however, is partly split into benzo-nitrile and HCl, while another part unites with the $POCl_3$ formed to form phosphuretted compounds like $C_6H_5CCl_2NHPOCl_2$ and $C_6H_5CCl : NPOCl_2$ (C. 1909, II. 814).

Benzamide bromide $C_6H_5CBr_2NH_2$, m.p. 70° (A. **140**, 307). **Benzamide iodide** $C_6H_5CI_2NH_2$ melts with decomposition (B. **25**, 2536) at 140°. It is produced when benzo-nitrile is poured into concentrated aqueous hydriodic acid.

Dimethyl-benzamide chloride $C_6H_5.CCl_2.N(CH_3)_2$, m.p. 36°, from the amide with phosgene or PCl_5. On heating, the dialkylated benzamide chlorides split off one or two molecules of chloralkyl and decompose into alkyl-benzimide chlorides and benzo-nitrile, the latter being partly polymerised to cyaphenin (B. **37**, 2812) :

$$C_6H_5CCl_2N(CH_3)_2 \xrightarrow{-CH_3Cl} C_6H_5CCl : NCH_3 \xrightarrow{-CH_3Cl} C_6H_5CN.$$

On the utilisation of this reaction for the breaking up of cyclic secondary bases, see Piperidin.

Benzanilide chloro-iodide $C_6H_5CClI.NNC_6H_5$, m.p. 106° with decomposition, from benzanilide-imido-chloride and HI (C. 1905, I. 442).

Methyl-benzimido-chloride $C_6H_5CCl : NCH_3$, from methyl-benzamide with PCl_5.

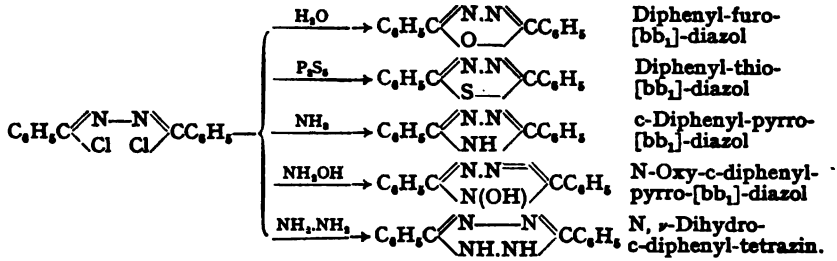
Benzanilide-imido-chloride $C_6H_5CCl : N.C_6H_5$, m.p. 40° and b.p. 310°, is produced when PCl_5 acts upon benzanilide (Wallach, A. **184**, 79), or upon benzo-phenone oxime $(C_6H_5)_2C{=}NCl$. Water or alcohol will decompose it into hydrochloric acid and benzanilide. For other transpositions of benzanilide-imido-chloride, compare thio-benzanilide, etc.

When benzanilide-imido-chloride acts upon sodium aceto-acetic ester, the products are anil-benzyl compounds, β-ketonic acid derivatives, which change to phenyl-quinolin-carboxylic acids upon the application of heat.

Benzo-phenyl-hydrazide-imido-chloride $C_6H_5CCl : N.NH.C_6H_5$, m.p. 131°, is formed when alcohol acts upon the reaction product of PCl_5 and sym. benzoyl-phenyl-hydrazin $C_6H_5.CCl : N.N(C_6H_5)POCl_2$ (B. **27**, 2122).

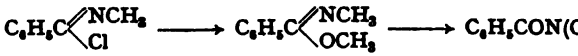
Dibenzo-hydrazide chloride $C_6H_5CCl : N.N : ClCC_6H_5$, m.p. 123°, from sym. dibenzoyl-hydrazin and PCl_5. It can easily be transformed into heterocyclic compounds :—(1) On boiling with water it yields diphenyl-furo-diazol ; (2) with P_2S_5, diphenyl-thio-diazol ; (3) with ammonia or primary amines, diphenyl-pyrro-diazols ; (4) with hydroxyl-

amine, N-oxy-diphenyl-pyrro-diazol; (5) with hydrazin, diphenyl-dihydro-tetrazin (*J. pr. Ch.* 2, **78**, 277):

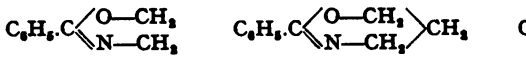


13. IMIDO-ETHERS OF THE AROMATIC ACIDS (Vol. I.)—The *imido-ethers* (their HCl salts) result from the action of HCl upon a mixture of a nitrile with an alcohol (Pinner, B. **16**, 1654; **21**, 2650; **28**, 2917). Their methyl sulphates are obtained by addition of dimethyl sulphate to primary and secondary acid amides.

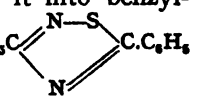
Water decomposes the HCl imido-ethers into acid esters and ammonium chloride. Benzalkyl-imido-chlorides, with sodium alcoholates, change into benzalkyl-imido-ethers. The latter are transposed into tertiary benzamides by the action of alkyl iodides or by heat (C. 1903, I. 833, 876):

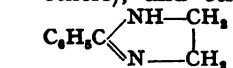


Sodium amalgam in acid solution reduces benzimido-ether to benzaldehyde (B. **35**, 3039). With ammonia the benzimido-ethers yield benzamidin (*q.v.*); with hydroxylamine, benzamidoxime; with hydrazin, benzenyl-hydrazidin (*q.v.*). The following bodies should be viewed as imido-ethers of aromatic carboxylic acids:

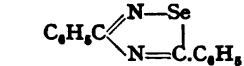


Benzimido-methyl ether $C_6H_5C(NH)OCH_3$, b.p.$_{12}$ 96°, and **benzimido-ethyl ether** $C_6H_5C(NH)OC_2H_5$, b.p.$_{15}$ 102°, are oils precipitated from their chlorohydrates by soda solution. The ethyl ether is also obtained from silver benzamide with ethyl iodide. Similarly, silver dibenzamide gives, with ethyl iodide, **benzol-benzimido-ethyl ether** $C_6H_5C(NCOC_6H_5)OC_2H_5$, m.p. 65° (C. 1898, I. 569). **n-Methyl-benzimido-methyl ether** $C_6H_5C(NCH_3)OCH_3$, b.p.$_{12}$ 94°.

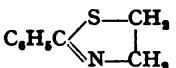
14. THIAMIDES OF THE AROMATIC ACIDS.—**Thio-benzamide** $C_6H_5.CS\,NH_2$ or $C_6H_5C(SH)NH$, melting at 116°, results on conducting hydrogen sulphide into an alcoholic solution of benzo-nitrile mixed with ammonia (B. **23**, 158), and when benzyl-amine is heated to 280° with sulphur (A. **259**, 304). Zinc and hydrochloric acid convert it into benzyl-amine, iodine into dibenzenyl-azo-sulphime (*q.v.*)  (B. **25**, 1588), ethylene bromide into μ-phenyl-thiazolin (see below), trimethylene bromide into μ-phenyl-penthiazolin (see Imido-

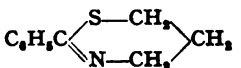
ethers), and ethylene-diamine into benzenyl-ethylene-diamine (*q.v.*)  (B. **25**, 2134). **Methyl-thio-benzamide** $C_6H_5CSNHCH_3$, m.p. 79°, from phenyl-magnesium bromide and methyl-mustard oil (B. **37**, 877).

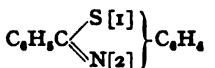
Thio-benzanilide $C_6H_5.CSNH.C_6H_5$, melting at 98°, consists of yellow plates or prisms. It is formed (1) when H_2S acts upon benzenyl-phenyl-amidine at 100°; (2) by the action of CS_2 at 110°, hydro-sulpho-cyanic acid being simultaneously produced (A. **192**, 29); (3) when H_2S acts upon benzanilide chloride; (4) when P_2S_5 acts upon benzamide; (5) from the interaction of phenyl-mustard oil, benzene, and aluminium chloride (B. **25**, 3525) (*J. pr. Ch.* 2, **59**, 572); (6) from phenyl-mustard oil and phenyl-magnesium bromide (B. **36**, 587). It is changed to benzyl-amido-thio-phenol by heat or oxidation.

Selenium benzamide $C_6H_5CSeNH_2$, m.p. 102°, golden needles, from benzo-nitrile and SeH_2. Iodine oxidises it to **dibenzenyl-azo-selenime**  (B. **37**, 2550).

15. IMIDO-THIO-ETHERS OF THE AROMATIC CARBOXYLIC ACIDS are obtained as chlorohydrates from nitriles, mercaptans, and hydrochloric acid (compare Imido-ethers). The following compounds must be considered as cyclic imido-thio-ethers of benzoic acid :


μ-Phenyl-thiazolin

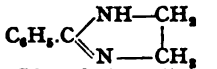

μ-Phenyl-penthiazolin

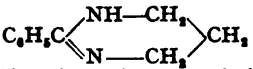

μ-Phenyl-benzo-thiazol.

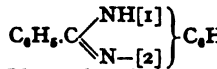
Benzimido-thio-ethyl ether $C_6H_5C(NH)S.C_2H_5$ is an oil. It readily resolves itself into benzo-nitrile and mercaptan (A. **197**, 348).

By heating sodium xanthogenates with benzalkyl-imido-chlorides in benzene solution the strongly red-coloured imido-xanthides are obtained: **Benzo-phenyl-amido-ethyl xanthide** $C_6H_5C(NC_6H_5)SCSOC_2H_5$, m.p. 98°, garnet-red prisms (B. **35**, 2470). **Benzimido-thio-phenyl ether** $C_6H_5C(NH)SC_6H_5$, m.p. 48° (B. **36**, 3465).

16. AMIDINES of aromatic monocarboxylic acids are obtained from nitriles, imido-ethers, imido-chlorides and thio-amides by means of ammonia and ammonium bases. The cyclic amidins correspond to the cyclic imido-ethers and imido-thio-ethers :


μ-Phenyl-glyoxalidin
Ethylene-benzamidin


m-Phenyl-tetrahydro-pyrimidin
Trimethylene-benzamidin


μ-Phenyl-benzimide-azol.

Benzamidine,* *benzenyl-amidine* $C_6H_5.C(NH)NH_2$, melting at 75°–80°, is formed from its *hydrochloride* $C_7H_8N_2.HCl+2H_2O$, consisting of vitreous crystals, melting at 72°, which, being anhydrous, become liquid at 169° (A. **265**, 130).

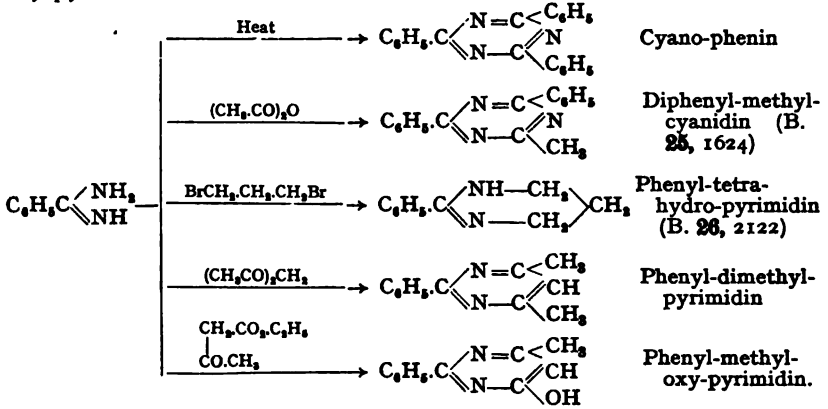
Silver salt $C_6H_5.C(=NAg)NH_2$. Benzamidine is a stronger base than ammonia. Hydroxylamine converts it, by an exchange of the NH group for the N(OH) group, into an amidoxime. Benzamidine

* *Die Imidoäther und ihre Derivate*, Pinner, 1892, p. 152.

gives with diazo-benzol : *benzamidine-diazo-benzol* (see below) ; with benzaldehyde : *benzal-benzamidine*, melting at 175° ; with phenyl-isocyanide : *benzenyl-diphenyl-diureïde* $C_6H_5C(:N.CONHC_6H_5).NHCO.NH.C_6H_5$, melting at 172° ; with phenyl-mustard oil : *benzamidin-phenyl-thio-urea* $C_6H_5.C(:NH).NH.CS.NH.C_6H_5$, melting at 125° ; with chloro-carbonic ether : *benzamidine-urethane* $C_6H_5.C(:NH).NHCO_2C_2H_5$, melting at 58° ; heat converts it into *diphenyl-oxy-cyanidin* ; with phosgene : *dibenzamidin-urea* $CO(NH.C(:NH.)C_6H_5)_2$, melting at 289°, and *diphenyl-oxy-cyanidin*.

The action of nitrous acid upon benzamidin is very remarkable. The product is *benzenyl-dioxy-tetrazotic acid* (see below).

Benzamidin Hetero-ring Formations.—Benzamidin heated alone becomes *cyano-phenin* ; heated with acetic anhydride the product is *diphenyl-methyl-cyanidin* ; with trimethylene bromide : *trimethylene-benzamidin*, or *μ-phenyl-tetrahydro-pyrimidin* ; with acetyl acetone : *phenyl-dimethyl-pyrimidin* ; with aceto-acetic ester : *phenyl-methyl-oxy-pyrimidin* :



Many other amidins besides benzamidin are known ; also numerous alkyl, phenyl, and benzyl substitution products of the simple amidins. As may be gathered from the description of benzamidin, the amidins are unusually reactive bodies, whose investigation has contributed much to the chemistry of the nitrogen-carbon ring systems.

Phenyl-benzamidin $C_6H_5C(NH)NHC_6H_5$, m.p. 114°, by the action of sodium upon a mixture of benzo-nitrile and aniline (*J. pr. Ch.* 2, **67**, 445). On the acidulation of phenyl-benzamidin and the accompanying transpositions, see C. 1903, II. 830.

Diphenyl-benzamidin $C_6H_5C(NC_6H_5)NHC_6H_5$, m.p. 144°, is a chromogen, yielding yellow dyes by the introduction of amido-groups (C. 1898, II. 1049). **Trialkyl-benzamidin**, see B. **37**, 2678.

17. Dioxy-tetrazotic Acids.—Free *benzenyl-dioxy-tetrazotic acid* $C_6H_5.C(N=N.OH)(N—NO)$ (?) is not known. Its benzamidin salt, melting at 178°, is produced when nitrous acid acts upon benzamidin. Sodium amalgam reduces the potassium salt to *benzenyl-oxy-tetrazotic acid* $C_7H_6N_4O+H_2O$, melting in anhydrous form at 175° with explosion,

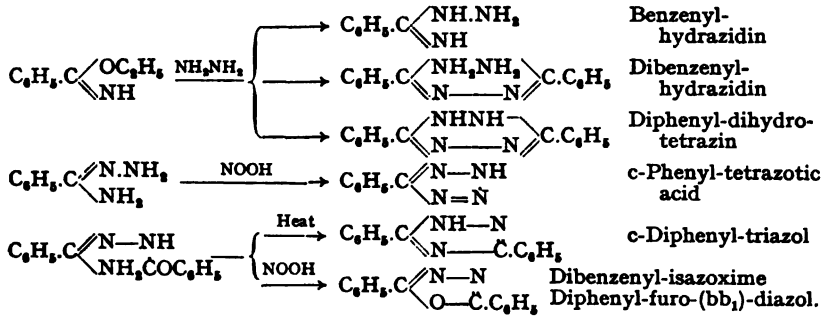
and *benzenyl-tetrazotic acid* (Lossen, A. **263**, 73; **265**, 129). These bodies belong to the class of heterocyclic tetrazols or pyrro-triazols.

18. HYDRAZIDINS OR AMIDRAZONES of aromatic monocarboxylic acids.—Several representatives of the aliphatic phenyl-hydrazidins were discussed in connection with phenyl-hydrazin. The simple aromatic hydrazidins result from the action of hydrazin upon the imido-ethers. The most thoroughly investigated is :

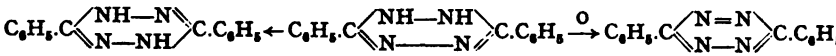
Benzenyl-hydrazidin $C_6H_5.C\begin{cases}NH.NH_2\\NH\end{cases}$ or $C_6H_5.C\begin{cases}N.NH_2\\NH_2\end{cases}$. This compound cannot be obtained from its salts in a pure condition. Its *benzoyl* derivative $C_6H_5C(:NH)NH.NH.CO.C_6H_5$ melts at 188°. It slowly parts with water, even at 120°, changing into c-diphenyl-triazol, whereas nitrous acid converts it into dibenzenyl-isaoxime or diphenyl-furo-(bb_1)-diazol.

In addition to benzenyl-hydrazidin, produced in the interaction of hydrazin and benzimido-ether, there also result :

Dibenzenyl-hydrazidin $C_6H_5.C(:NH).NH.NH(NH:)C.C_6H_5$ or $C_6H_5C(NH_2):N—N:(NH_2)C:C_6H_5$, melting at 202°, and *diphenyl-dihydro-tetrazin* (*q.v.*). Nitrous acid changes benzenyl-hydrazidin into *phenyl-tetrazotic acid* (*q.v.*) :



Diphenyl-dihydro-tetrazin is readily rearranged by acids into **iso-diphenyl-dihydro-tetrazin.** It oxidises on exposure to the air to diphenyl-tetrazin (Pinner, B. **27**, 3273; **28**, 465; A. **297**, 221; **298**, 1) :



19. NITRAZONES, NITROSAZONES OR PHENYL-AZOXIMES.—These derivatives of the benzoic acids are obtained by the same methods as are the corresponding aliphatic derivatives.

Benzenyl-nitrazone, *phenyl-nitro-formaldehydrazone,* $C_6H_5C\begin{cases}NO_2\\NNHC_6H_5\end{cases}$ and $C_6H_5C\begin{cases}NOOH\\N:NC_6H_5\end{cases}$, m.p. 102°, is formed from phenyl-nitro-methane, or from nitro-methane itself, by the action of diazo-benzol. It is best obtained from benzaldehyde-phenyl-hydrazone with amyl nitrite or N_2O_4 (C. 1908, II. 945); an intermediate product is **benzenyl-nitrosazone** $C_6H_5C(NO):NNHC_6H_5$, with its more stable transposition product, **phenyl-azo-benzaldoxime** $C_6H_5C\begin{cases}NOH\\N:NC_6H_5\end{cases}$, m.p. 135°. This is obtained from benzaldehyde-phenyl-hydrazone with amyl nitrite and pyridin. Reduction with Am_2S converts phenyl-

nitro-formaldehydrazone first into **phenyl-hydrazo-benzaldoxime** $C_6H_5C(NOH)NHNHC_6H_5$, and this is oxidised by ferric chloride to phenyl-azo-benzaldoxime. The **methyl ester of phenyl-nitro-formaldehydrazone** $C_6H_5C(NOOCH_3):NNHC_6H_5$, m.p. 92°, breaks up, on boiling with alcohol, into formaldehyde and phenyl-azo-benzaldoxime (B. **34,** 2019; **35,** 1091; **36,** 62, 90). **m-Nitro-benzenyl-nitrosazone** $NO_2C_6H_4C(NO):NNHC_6H_5$, m.p. 98° with decomposition, is transposed by sodium ethylate, or pyridin, into **phenyl-azo-m-nitro-benzaldoxime** $NO_2C_6H_4C(NOH).N:NC_6H_5$, m.p. 183° with decomposition. The nitrosazones easily lose nitric oxide, even when boiled with ether, and the residues undergo various condensations (B. **36,** 92).

20. FORMAZYL DERIVATIVES OF THE AROMATIC MONOCARBOXYLIC ACIDS.—**Formazyl-benzol** $C_6H_5C\begin{cases}N=N.C_6H_5\\N\text{——}NH.C_6H_5\end{cases}$, m.p. 173°, consists of red flakes with a greenish metallic reflex. It is produced (1) when diazo-benzol in alkaline solution (B. **27,** 1690) acts upon benzaldehyde-phenyl-hydrazone; (2) from benzenyl-amidoxime and phenyl-hydrazin (B. **27,** 160); (3) when phenyl-hydrazin and benzo-phenyl-hydrazide-imide chloride interact. The hetero-ring formations of the formazyl compounds have been described. A glacial acetic acid solution of sulphuric acid converts formazyl-benzol into **pheno-phenyl-triazin** (*q.v.*). It yields **triphenyl-tetrazolium hydroxide** upon oxidation:

$$C_6H_5.C\begin{cases}N=N.C_6H_5\\N\text{—}NHC_6H_5\end{cases}\begin{cases}\xrightarrow{-C_6H_5NH_2} C_6H_5C\begin{cases}N=N\text{—}[1]\\N\text{——}[2]\end{cases}C_6H_4 & \text{Phene-phenyl-triazin}\\ \xrightarrow{+O} C_6H_5C\begin{cases}N=N(OH)C_6H_5\\N\text{—}NC_6H_5\end{cases} & \text{Triphenyl-tetrazolium-hydroxide.}\end{cases}$$

Guanazyl-benzol $C_6H_5C\begin{cases}N.NHC(NH_2):NH\\N:NC_6H_5\end{cases}$, orange-yellow prisms, melting at 199°. It is formed when diazo-benzol chloride acts upon benzal-amido-guanidin, the condensation product derived from benzaldehyde and amido-guanidin. Nitric acid oxidises guanazyl-benzol to diphenyl-tetrazol (B. **30,** 444).

21. HYDROXAMIC ACIDS, THEIR ETHERS AND ESTERS.—Under benzamide mention was made of the two structural formulæ which were theoretically possible for benzamide: the *benzamide* formula and the *benzimido-acid* formula. If we suppose, in these formulæ, a hydrogen atom in union with nitrogen to be replaced by the hydroxyl group, we arrive at the two formulæ theoretically possible for a hydroxamic acid:

$$C_6H_5.C\begin{cases}NH_2\\O\end{cases}\quad\text{or}\quad C_6H_5C\begin{cases}NH\\OH\end{cases};\qquad C_6H_5C\begin{cases}NHOH\\O\end{cases}\quad\text{or}\quad C_6H_5C\begin{cases}NOH\\OH\end{cases}$$

Benzamide — Benzo-hydroxamic acid.

The amido-formula is preferred for the amides of the carboxylic acids; the imido-ethers are derived from the imido-acid formula. The oximido-acid formula is, however, more probable for the benzo-hydroxamic acids. *Hydroxime-acid chlorides* correspond to the imide chlorides, and *amidoximes* to the amidines. Although hydroxamic acid, and its homologues, are known in but one form each, many ethereal derivatives of the hydroxamic acids occur in several similarly constituted modifications, whose observed difference can in no satisfactory

way be attributed to structural difference (W. Lossen, A. **281,** 169). Just as in the case of the oximes, so here the isomeric phenomena of benzo-hydroxamic acid ethers are referred to the stereo-chemistry of nitrogen.

α- and β-Ethyl-benzo-hydroxamic acids differ from each other by the following space-formulas (Werner, B. **25,** 33) :

$C_6H_5.C(OC_2H_5)(HON)$ Ethyl-syn-benzo-hydroxamic acid (α-)

$C_6H_5.C(OC_2H_5)(N.OH)$ Ethyl-anti-benzo-hydroxamic acid (β-).

Crystallographic studies have shown that many classes of amide-like derivatives of hydroxylamine appear in polymorphous modifications.

Benzo-hydroxamic acid $C_6H_5.C(:NOH).OH$, m.p. 124°, and **dibenzo-hydroxamic acid** or **benzoyl-benzo-hydroxamic ester** $C_6H_5C(:NO.COC_6H_5)OH$, m.p. 161°, are produced by the interaction of benzoyl chloride and hydroxylamine. Benzo-hydroxamic acid is also formed by oxidation of benzaldoxime with Caro's acid; from phenyl-nitro-methane $C_6H_5CH_2NO_2$; by isomerisation by means of alkali; from benzaldehyde by transposition with benzol-sulphydroxamic acid, or with nitro-hydroxylaminic acid (B. **34,** 2023; **35,** 51; C. 1901, II. 99, 770; 1904, I. 24). If silver benzoate is made to act upon benzo-hydroximic chloride, an isomer of dibenzo-hydroxamic acid is first formed, melting at 95°, and this easily transposes into an isomer of higher m.p., incidentally splitting off benzoic acid, and forming a certain quantity of diphenyl-furoxane. A few substituted benzo-hydroximic chlorides only yield the corresponding diphenyl-furoxanes (B. **32,** 1654). On heating benzo-hydroxamic acid with thionyl chloride in benzene solution, we get phenyl iso-cyanate, with intramolecular atomic displacement (C. 1907, I. 633) :

$$C_6H_5C(:NOH)OH+SOCl_2 = C_6H_5N:C:O+SO_2+2HCl.$$

The potassium salt of the dibenzo-hydroxamic acid is decomposed by water, especially on heating, into potassium benzoate, s-diphenyl-urea, and CO_2 :

$$2C_6H_5C(:NOCOC_6H_5).OK+H_2O = 2C_6H_5COOK+CO(NHC_6H_5)_2+CO_2.$$

Other acidyl derivatives of benzo-hydroxamic acid behave similarly; on heating with ammonia they yield monophenyl-urea; with alcohol, phenyl-urethane,—*i.e.* transformation products of phenyl iso-cyanate (A. **309,** 189).

The rearrangement occurring here recalls that of ketoximes (Beckmann, p. 189) to alkylised acid amides. As s-diphenyl-urea can be resolved by hydrochloric acid into aniline and CO_2, it is possible, aided by these reactions, which are capable of greater generalisation, to change benzoic acid to aniline—that is, to replace the CO_2H group by the NH_2 group (A. **175,** 313; compare benzoyl azide). The alkyl ethers of dihydroxamic acid are known in two modifications: **α-(syn)-methyl ether,** m.p. 53°; **β-(anti)-methyl ether,** m.p. 55°; **α-(syn)-ethyl ether,** m.p. 58°; **β-(anti)-ethyl ether,** m.p. 63° (A. **205,** 281; **281,** 235). The α-bodies result from the action of alkyl iodides upon the silver salts; the β-compounds through the action of benzoyl chloride and caustic potash upon the alkyl-hydroximic acids.

Benzo-hydroximic acid alkyl ethers or **alkyl-benzo-hydroximic**

acids $C_6H_5C(:NOH)OR'$ are obtained from benzimido-ethers and hydroxylamine hydro-chloride, and from dibenzo-hydroxamic acid alkyl ethers (A. **252,** 211). They occur in two modifications, which can be distinguished by the fact that the α- or syn-modifications yield on treatment with PCl_5 (by Beckmann's transposition) phenyl-carbamic acid ethers, or their transposition products :

$$\begin{matrix} C_6H_5COCH_3 \\ HO\ N \end{matrix} \longrightarrow \begin{matrix} OCOCH_3 \\ C_6H_5NH \end{matrix},$$

whereas the β- or anti-forms become phosphoric ethers of the alkyl-benzo-hydroximic acids (B. **29,** 1146). **α-(syn)-Methyl ether,** m.p. 64°, readily changes to a physical isomeride, also belonging to the syn-modification, m.p. 101° (B. **29,** 1150). **β-(anti)-Methyl ether,** m.p. 44°; **α-(syn)-ethyl ether,** m.p. 53°; and **β-(anti)-ethyl ether,** m.p. 68°.

The alkyl-benzo-hydroximic acids also form alkyl and acidyl ethers. **Tribenzoyl-hydroxylamine** $C_6H_5.C(:NOCOC_6H_5)O.COC_6H_5$ is produced in three forms when benzoyl chloride acts upon hydroxylamine chloro-hydrate : α-modification, m.p. 100°; β-modification, m.p. 141°; and the γ-modification, m.p. 112°. Hydrochloric acid changes the α- and γ-modifications into the β-form (A. **281,** 276).

Thio-benzo-hydroxamic acid $C_6H_5C\begin{matrix}SH\\NOH\end{matrix}$, an unstable oil, is formed by the action of hydroxylamine upon dithio-benzoic acid. The di-benzoyl compound melts at 92° (C. 1909, II. 1552).

22. Haloids of Benzo-hydroxamic Acid.—The free chlorides, as well as the ethers of the fluorides, chlorides, and bromides, are known. The free chlorides result from the corresponding benzaldoximes upon treatment with chlorine in chloroform solution. The ethers are produced when the amidoxime ethers are treated with haloid acids and an alkaline nitrite; also when PCl_5 acts upon the alkyl ethers of hydroxamic acid (A. **252,** 217). The hydroximic chlorides with ammonia yield *amidoximes*; with hydroxylamine, hydroxam-oximes; on standing, or, rapidly, on heating, they are decomposed to form azoximes (*q.v.*) and nitriles; with sodium carbonate they split off HCl and yield nitrile oxides. For transposition with silver salts, see B. **32,** 1975.

Benzo-hydroximic acid chloride $C_6H_5C(:NOH)Cl$, melting at 48°, from benzaldoxime, is converted by ammonia into benzenyl-amidoxime (B. **27,** 2193, 2846). **Benzenyl-methoxime chloride** $C_6H_5.C(:NOCH_3)Cl$, boils at 225°. **Benzenyl-ethoxime bromide** $C_6H_5.C(:NOC_2H_5)Br$ boils at 239° (B. **24,** 3454).

Benzenyl-hydroxylamine-acetic acid $C_6H_5.C(:NOCH_2.CO_2H).OH$, melting at 135°–138°, is formed when caustic potash acts upon benzenyl-nitroxime-acetic acid $C_6H_5.C(:NO.CH_2CO_2H)ONO$, melting at 95°. The latter is produced through the action of sulphuric acid and potassium nitrite upon benzenyl-amidoxime-acetic acid (see below). **Benzenyl-fluor-, chlor-,** and **bromoxime-acetic acids** all melt at 135°. They are obtained when haloid acids and an alkaline nitrite are allowed to act upon benzenyl-amidoxime-acetic acid (B. **26,** 1570).

23. Benzo-nitrolic Acid $C_6H_5C\begin{matrix}NOH\\NO_2\end{matrix}$, light-yellow needles, of very bitter taste, m.p. 58°, is formed, besides benzaldoxime peroxide, by the action of HNO_2 upon phenyl-iso-nitro-methane, and, in small

quantity, by oxidation of benzo-nitrosolic acid with $KMnO_4$ (B. **39**, 2522). It is much more unstable than the paraffin-nitrolic acids, and easily decomposes on standing, doing so instantly on heating with HNO_2 and *diphenyl-furoxane* (*q.v.*), with intermediate formation of *benzo-nitrile oxide*. In alkalies it dissolves with an orange coloration. The solutions of the alkali salts decompose spontaneously into alkali nitrite and tribenzo-nitrile oxide.

24. BENZO-NITROSOLIC ACID $C_6H_5C\begin{matrix}NOH\\NO\end{matrix}$ is obtained in the form of its dark-blue salts, by the action of aqueous alkalies, or ammonia, upon benzo-hydroxame oxime, with intermediate formation of the very unstable red azo-compound $C_6H_5C\begin{matrix}NOH\ HON\\N{=}{=}N\end{matrix}CC_6H_5$, which is split up, by hydrolysis, into benzenyl-amidoxime and benzo-nitrosolic acid. The free acid is not stable; liberated from its salts, it decomposes into HNO_2 and benzo-nitrile. The action of iodine upon the silver salt (pink needles, decomposing at 94°) produces *diphenyl-furoxane* (B. **39**, 1480).

25. NITRILE OXIDES.—The nitrile oxides contain the atomic group $-C\begin{matrix}N\\|\\O\end{matrix}$ and may therefore be regarded as anhydrides of the hydroxamic acids, with which they are in close genetic connection.

Benzo-nitrile oxide $C_6H_5C\begin{matrix}N\\|\\O\end{matrix}$ forms a mobile oil, of a penetrating odour, resembling nitrile. At a low temperature it solidifies in a crystalline mass, melting at 15°. It is obtained by withdrawing HCl from benzo-hydroximic chloride by means of sodium carbonate (B. **40**, 1667). On keeping, it quickly polymerises to *diphenyl-furoxane* $C_6H_5.C\begin{matrix}-C-C_6H_5\\N.O.N-O\end{matrix}$. On heating in xylol solution it partly isomerises to phenyl iso-cyanate (B. **42**, 4207). Concentrated HCl splits it up into benzoic acid and hydroxylamine, while zinc dust and glacial acetic acid reduce it to benzo-nitrile. With methyl-magnesium iodide it combines to form aceto-phenone oxime:

$$C_6H_5C\begin{matrix}N\\|\\O\end{matrix} \xrightarrow{CH_3MgI} C_6H_5C(:NOMgI)CH_3 \xrightarrow{HCl} C_6H_5C(:NOH)CH_3.$$

A trimeric body of benzo-nitrile oxide is formed by the spontaneous decomposition of an aqueous solution of sodium benzo-nitrolate, with splitting off of sodium nitrite.

Tribenzo-nitrile oxide $\left(C_6H_5C\begin{matrix}N\\|\\O\end{matrix}\right)_3$ is decomposed at 130°, with explosion when rapidly heated. In its transformations it resembles the monomeric compound. Heating in toluol solution depolymerises it, with formation of phenyl iso-cyanate; with aniline, it yields diphenyl-urea, by reduction, benzo-nitrile. Alcoholic HCl splits it, partly into benzoic acid and hydroxylamine, and partly transforms it into *dibenzenyl-azoxime* $\begin{matrix}N.O.C-C_6H_5\\C_6H_5C-N-O\end{matrix}$ (B. **42**, 806).

26. THE AMIDOXIMES are produced by the action of hydroxylamine upon thio-amides, nitriles, imido-ethers, and amidines. Ferric chloride imparts a deep-red colour to the alcoholic solution of the amidoximes.

Benzenyl-amidoxime, amide of benzo-hydroxamic acid $C_6H_5.C\langle^{N(OH)}_{NH_2}$, melts at 79°. It gives the iso-nitrile reaction with chloroform and potassium hydroxide. Nitrous acid changes it to benzamide. With acids and caustic alkalies it yields salts—*e.g.* $C_6H_5.C(:N.OH)NH_2.HCl$ and $C_6H_5.C(NH_2):N.OK$. Alkyl iodides convert the latter into amidoxime ethers.

Methyl ether $C_6H_5(.NH_2):NOCH_3$ melts at 57°; the **ethyl ether** melts at 67° (A. **281,** 280).

Acetyl-benzenyl-amidoxime $C_6H_5.C(:NOCOCH_3).NH_2$ melts at 16° (B. **18,** 1082). **Benzenyl-oximido-carbonic ester** $C_6H_4C(.NH_2):NOCO_2C_2H_5$ melts at 127°. **Benzenyl-oximido-glycollic acid** $C_6H_5.C(.NH_2):NO.CH_2.CO_2H$ melts at 123°. **Benzenyl-amidoxime-butyric acid** $C_6H_5C(NH_2):NOCH(C_2H_5)COOH$ melts at 82° (B. **29,** 2655).

Hetero-ring Formations of the Amidoximes.—(1) The amidoximes condense with the aldehydes of the fatty series to *hydrazoximes.* The amidoxime acid derivatives, alluded to above, throw off, on heating above their melting-points, water or alcohol, and become *azoximes* :

$C_6H_5.C\langle^{NH_2}_{NOH} \xrightarrow[-H_2O]{+CH_3CHO} C_6H_5.C\langle^{NH\text{—}}_{N\text{—}O}\rangle CH.CH_3$ Benzenyl-hydrazoxime-ethidene

$C_6H_5.C\langle^{NH_2}_{N.O.COCH_3} \xrightarrow{-H_2O} C_6H_5.C\langle^{N=}_{N\text{—}O}\rangle C.CH_3$ Ethenyl-benzenyl-azoxime

$C_6H_5.C\langle^{NH_2}_{N.O.CH_2.CO_2H} \xrightarrow{-C_2H_5OH} C_6H_5.C\langle^{NH\text{—}}_{N\text{—}O}\rangle CO$ Carbonyl-benzenyl-azoxime

$C_6H_5.C\langle^{NH_2}_{N.O.CH_2.CO_2H} \xrightarrow{-H_2O} C_6H_5.C\langle^{NH\text{—}CO}_{N\text{—}O}\rangle CH_2$ Benzenyl-amidoxime-glycollic acid.

There is a distinction between the amidoximes and the oxy-amidins, which have the same tautomeric fundamental form :

$$-C\langle^{NOH}_{NH_2} \quad \text{and} \quad -C\langle^{NHOH}_{NH}.$$

Oxy-amidins are produced from imido-chloride with β-aryl-hydroxylamines (B. **34,** 2620; **36,** 18). **Benzenyl-phenyl-p-tolyl-oxy-amidin** $C_6H_5C(NC_6H_5)N(C_7H_7)OH$, m.p. 175°, and **benzenyl-p-tolyl-phenyl-oxy-amidin** $C_6H_5C(NC_7H_7)N(C_6H_5)OH$, m.p. 191°, on reduction with H_2SO_3, form the same phenyl-tolyl-benzamidin.

27. HYDRAZIDOXIMES result from benzo-hydroximic chloride, and hydrazin hydrate, in alcoholic solution. Like the amidoximes, they possess an amphoteric character, and dissolve in acids as well as in alkalies. The latter readily decompose them, with liberation of nitrogen.

Benzenyl-hydrazidoxime $C_6H_4C\langle^{NOH}_{NHNH_2}$, m.p. 110° with decomposition, yields N-oxy-c-phenyl-tetrazol with nitrous acid. With benzaldehyde it condenses to **benzal-benzenyl-hydrazidoxime** $C_6H_5C(:NOH)NH.N:CHC_6H_5$, m.p. 120°, which, with acids, is easily anhydrated into cc_1-diphenyl-triazol (B. **42,** 4199) :

$C_6H_5C\langle^{NOH}_{NH\text{—}NH_2} \xrightarrow{NOOH} C_6H_5C\langle^{N(OH).N}_{N\text{———}N}$ N-Oxy-c-phenyl-tetrazol

$C_6H_5C\langle^{NOH}_{NH.N=CHC_6H_5} \xrightarrow{-H_2O} C_6H_5C\langle^{N\text{———}}_{NH.N=CC_6H_5}$ c,c_1-Diphenyl-triazol.

28. HYDROXAMOXIMES.—**Benzo-hydroxamoxime,** *benzenyl-oxy-amidoxime* $C_6H_5C(NOH)NHOH$, m.p. 115° with decomposition, is formed from benzo-hydroximic chloride with hydroxylamine; it yields a reddish-brown copper salt $(C_7H_7N_2O_2)_2Cu$ (B. **31,** 2126). Alkalies convert it into a red azo-body, which is further hydrolysed to benzenyl-amidoxime and the salts of benzo-nitrosolic acid (B. **39,** 1480).

DERIVATIVES OF ORTHOBENZOIC ACID.

29. **Ethyl-orthobenzoic ester,** *ethyl ortho-benzoate, benzenyl-ethyl Ether* $C_6H_5C(O.C_2H_5)_3$, from phenyl-chloroform and sodium ethylate, boils at 220°–225°, or from phenyl-magnesium bromide and ortho-carbonic ester (B. **38,** 564).

30. **Benzo-trichloride,** *phenyl-chloroform, benzoic acid trichloride, benzenyl trichloride* $C_6H_5CCl_3$, melting at —22·5° (B. **26,** 1053), boiling at 213°, with sp. gravity 1·38 (1°4), is isomeric with the chloro-benzal chlorides, dichloro-benzyl chlorides, and the trichloro-toluenes. Phenyl-chloroform bears the same relation to benzoic acid or phenyl-formic acid that methyl-chloroform bears to acetic acid or methyl formic acid (I. 256). It results (1) upon conducting chlorine into boiling toluol, until there is no further increase in weight (A. **146,** 330); (2) by the action of phosphorus pentachloride upon benzyl chloride (A. **139,** 326). It changes to benzoic acid when heated to 100° with water. It yields benzoyl chloride and benzoic anhydride on being digested with anhydrous oxalic acid (A. **226,** 20). It readily condenses to triphenyl-methane derivatives, with the anilines and phenols (B. **15,** 232; A. **217,** 223).

Benzo-trifluoride $C_6H_5CF_3$, b.p. 103°, is formed besides **difluoro-chloro-toluol** $C_6H_5CClF_2$, b.p. 143°, from benzo-trichloride and antimony trifluoride (C. 1898, II. 26).

31. **Ortho-benzoic acid piperidide** $C_6H_5C(N.C_5H_{10})_3$, m.p. 80°, is produced on warming benzo-trichloride and piperidin.

The *benzamide haloids* also belong to the derivatives of ortho-benzoic acid.

(*c*) SUBSTITUTED AROMATIC MONOCARBOXYLIC ACIDS.

Only those will be given in connection with the monocarboxylic acids in which the substitution has occurred with the hydrogen atoms of the benzene nucleus. Certain ortho-products show the power, by water elimination, of yielding inner anhydrides or heterocyclic compounds.

See above for the behaviour of 2, 6-substituted carboxylic acids in their esterification with alcohol and hydrochloric acid.

1. **Halogen Benzoic Acids** are formed:

(1) By the substitution of benzoic acids or nitriles; the halogen atom entering first prefers the meta-position with reference to carboxyl.

(2) By oxidising p- and m-halogen toluols and higher homologues with chromic acid, and o-haloid hydrocarbons with dilute nitric acid or potassium permanganate. In the animal organism the halogen toluols are transformed with the corresponding halogen-substituted hippuric acids (C. 1903, I. 411).

(3) From the amido-acids by means of (*a*) the diazo-sulphates, or (*b*) the diazo-amido-acids; both classes, when boiled with haloid acids, have been obtained from the diazo-amido-benzoic acids (B. **15,** 1197).

(4) By the action of phosphorus pentachloride upon the oxy-acids (compare salicylic acid).

(5) Nuclear synthesis: heating the halogen nitro-benzols to 200°–230° with potassium cyanide and alcohol. In this reaction the cyanogen group replaces the nitro-group; it does not, however, take the same position in the benzene residue (B. **8,** 1418). At the temperature of the reaction the nitrile changes to the acid. m-Chloro-nitro-benzol yields o-chloro-benzoic acid; and p-chloro-nitro-benzol, m-chloro-benzoic acid.

(6) From the haloid anilines through the diazo-compounds, etc.

Properties and Behaviour.—In the following tabulation of the melting-points of the monohaloid benzoic acids it will be observed that the ortho-bodies melt at the lowest temperatures, and the para-compounds at the highest. The melting-point rises with the atomic mass of the substituting halogen. The ortho-derivatives are fairly readily soluble in water, and easily yield soluble barium salts, whereby they can usually be quite readily separated from the meta- and para-derivatives. When they are fused with caustic potash, oxy-benzoic acids result. With NH_3, or amines and copper, o-chloro-benzoic acid is transposed into anthranilic acid and n-alkyl-anthranilic acids (A. **355,** 312).

Fluoro-benzoic acid :	o-, m.p. 120° :	m-, m.p. 124° ;	p-, m.p. 182°
Chloro-benzoic acid :	o-, „ 137° ;	m-, „ 153° ;	p-, „ 240°
Bromo-benzoic acid :	o-, „ 147° :	m-, „ 155° ;	p-, „ 251°
Iodo-benzoic acid :	o-, „ 162° ;	m-, „ 187° ;	p-, „ 265°.

Numerous poly-chloro- and poly-bromo-benzoic acids are known. The five hydrogen atoms of the phenyl of benzoic acid can be replaced by chlorine or bromine.

2. **Iodoso- and Iodo-benzoic Acids.**—Upon chlorinating the three iodo-benzoic acids in chloroform, three iodo-chloro-benzoic acids are produced. Sodium hydroxide changes these to the iodoso-benzoic acids (B. **27,** 2326). **o-Iodoso-benzoic acid** $C_6H_4(IO)CO_2H$ consists of brilliant flakes, which explode at 244°. This acid is also produced in the oxidation of o-iodo-benzoic acid with fuming nitric acid (B. **28,** 83), and together with **o-iodo-benzoic acid** $C_6H_4(IO_2)CO_2H$, exploding at 230° with violence, when o-iodo-benzoic acid is oxidised with potassium permangate. The formula $C_6H_4\begin{cases}[1]I(OH)\\ [2]CO\end{cases}\!\!>O$ has also been suggested for the o-iodoso-benzoic acid, as it yields, like lævulinic acid, when heated with acetic anhydride, an acetyl derivative: **acetiodoso-benzoic acid** $C_6H_4\begin{cases}[1]I(OCOCH_3)\\ [2]CO\end{cases}\!\!>O$, melting at 166° (B. **26,** 1364).

3. **Nitro-monocarboxylic Acids.**—Not more than three nitro-groups have been introduced into the benzene residue of an aromatic carboxylic acid.

Nitro-benzoic Acids.—(1) Meta-nitro-benzoic acid is the principal product in the nitration of benzoic acid. The quantity of the ortho- (20 per cent.) and para- (1·8 per cent.) acids is less (A. **193,** 202). (2) By oxidising the three nitro-toluols; the ortho- with potassium permangan-

ate (B. **12,** 443), and the meta- and para- with a chromic acid mixture (A. **155,** 25). o- and p-Nitro-benzoic acids are also produced by oxidising o- and p-nitro-benzyl chloride with potassium permanganate (B. **17,** 385), as well as by oxidising o- and p-nitro-cinnamic acids. (3) By converting the three isomeric nitranilines into the three nitro-benzo-nitriles (B. **28,** 150). The nitration of o-benzo-nitrile yields m-nitro-benzo-nitrile almost exclusively. o-Nitro-benzo-nitrile has been obtained from o-nitraniline (B. **28,** 151). Nitro-acids result upon saponifying the nitro-nitriles with caustic soda :

o-Nitro-benzoic acid	melts at 147° ;	*o-Nitro-benzo-nitrile*	melts at 109°
m-Nitro-benzoic acid	„ 141° ;	*m-Nitro-benzo-nitrile*	„ 116°
p-Nitro-benzoic acid	„ 238° ;	*p-Nitro-benzo-nitrile*	„ 147°.

o-Nitro-benzoic acid possesses a sweet taste, and dissolves in 164 parts of water at 16°. Its nitration produces 2, 6-, 2, 5-, 2, 4-dinitro-benzoic acids, and styphnic acid. o-Nitro-benzoyl chloride, m.p. 25°, see C. 1901, I. 1227. m-Nitro-benzoic acid dissolves in 425 parts of water (16°). Its barium salt dissolves with difficulty. Upon nitration it yields 2, 5-dinitro-benzoic acid. p-Nitro-benzoic acid (chloride, m.p. 75° ; anhydride, m.p. 190° ; see A. **314,** 305), called also *nitro-dracrylic acid,* because it is formed in the action of nitric acid upon dragon's blood (A. **48,** 344), is very sparingly soluble in water. Nitration converts it into 2, 4- and 3, 4-dinitro-benzoic acids. The electrolysis of its warm sulphuric acid solution produces p-amido-phenol-sulphonic acid (B. **28,** R. 378 ; compare also B. **28,** R. **126**). 2, 4-, 3, 4-Dinitro- and 2, 4, 6-trinitro-benzoic acids are obtained by the oxidation of the corresponding nitro-toluols. The dinitro-toluols are oxidised by a chromic acid mixture (B. **27,** 2209), or by potassium permanganate. Trinitro-toluol is oxidised by a nitric-sulphuric acid mixture at 150°–220°.

2, 4-Dinitro-benzoic acid melts at 179° ; the 2, 5-acid melts at 177° ; 2, 6-acid at 202° ; the 3, 4-acid at 165° ; the 3, 5- or *ordinary* dinitro-benzoic acid melts at 204°. **2, 4, 6-Trinitro-benzoic acid** $(NO_2)_3C_6H_2CO_2H$ melts at 210° with the elimination of CO_2 (B. **27,** 3154 ; **28,** 2564, 3065, R. 125 ; C. 1899, II. 98). **Chlorimido-m-nitro-benzoic methyl ester** $NO_2[3]C_6H_4C\langle^{NCl}_{OCH_3}$ is formed from benzoyl chloramide and diazo-methane ; it occurs in two stereo-isomeric forms, m.p. 88° and 84° ; gaseous HCl reduces both to the same **m-nitro-benz-imido-methyl ester** $NO_2C_6H_4C(:NH)OCH_3$, from which sodium hypochlorite restores a mixture of the two isomers (C. 1908, II. 1174).

Nitro-haloid benzoic acids (C. 1901, II. 287 ; 1902, II. 581).— **o, o-Fluo-nitro-benzoic acid** $C_6H_3F(NO_2)COOH$, melting at 127°, has been prepared by oxidising fluo-nitro-toluol. In contrast with the other o, o-di-substituted benzoic acids, it can be quite readily esterified (B. **29,** 842). **1, 4, 6-Mononitro-chloro-benzoic acid,** m.p. 165°, and two **dinitro-chloro-benzoic acids,** m.p. 238° and 200°, are formed by nitrifying o-chloro-benzoic acid (C. 1900, I. 742). The nitration of m-bromo-benzoic acid yields two o-nitro-acids, both of which yield anthranilic acid upon reduction : 3-bromo-2-nitro-benzoic acid, melting at 250°, and 3-bromo-6-nitro-benzoic acid, melting at 139° (compare equivalence of the six hydrogen atoms of benzene). The halogen atom

in the nitro-haloid benzoic acids is reactive, like that in the nitro-haloid benzols (B. **22,** 3282).

Nitro-phenyl-acetic acids $NO_2.C_6H_4.CH_2.CO_2H$ are produced by saponifying the nitro-benzyl-cyanides with caustic alkali. The latter bodies constitute the product resulting from the action of potassium cyanide upon the nitro-benzyl chlorides (B. **16,** 2064; **19,** 2635). The nitration of phenyl-acetic acid produces chiefly the p-nitro-body, with little of the o-nitro-acid and o, p-dinitro-phenyl-acetic acid, melting at 166°. The latter is also obtainable from 2, 4-dinitro-phenyl-aceto-acetic ester, by saponification with dilute H_2SO_4 (B. **42,** 601).

o-, m-, p-Nitro-phenyl-acetic acid, m.p. 141°, 120°, 152°
o-, m-, p-Nitro-benzyl cyanide ,, 84°, 61°, 116°.

Nitro-hydro-cinnamic acids $NO_2C_6H_4CH_2.CH_2.CO_2H$.—p-Nitro- and o-nitro-hydro-cinnamic acids result from the nitration of hydro-cinnamic acid. Both, in turn, yield the o, p-dinitro-acid. The o-nitro-acid is also prepared from o-nitro-p-amido-hydro-cinnamic acid, the first reduction product of the o, p-dinitro-acid, as well as from o-nitro-benzyl-malonic ester (*q.v.*). The m-nitro-acid is obtained from p-acet-amido-m-nitro-hydro-cinnamic acid (B. **15,** 846; **29,** 635; compare also m-nitro-toluol).

o-, m-, p-Nitro-hydro-cinnamic acid, m.p. 115°, 118°, 163°
o, p-Dinitro-hydro-cinnamic acid, ,, 123° (B. **13,** 1680).

o- and **p-Nitro-hydratropic acids** $NO_2.C_6H_4.CH(CH_3).CO_2H$, m.p. 110° and 87°, are produced upon introducing hydratropic acid into strongly cooled fuming nitric acid (A. **227,** 262).

4. **Nitroso-monocarboxylic Acids.—o-Nitroso-benzoic acid** $C_6H_4[1]NO[2]CO.OH$, melting with decomposition at 210°. It consists of colourless crystals, green in solution, and is formed from anthranilic acid by oxidation with Caro's acid (B. **36,** 3651), and from o-nitro-benzaldehyde by transposition under illumination in indifferent solvents. In alcoholic solutions we obtain the esters: **methyl ester,** m.p. 153°; **ethyl ester,** m.p. 121° (A. **371,** 319). **o-Nitro-benzylidene-aniline** $C_6H_4[1]NO_2[2]CH:NC_6H_5$, in light gives **o-nitroso-benz-anilide** $C_6H_4(NO)CONHC_6H_5$ (B. **35,** 2715; **36,** 4373). In connection with these modes of formation, we have the formation of o-nitroso-benzoic acid by the action of alcoholic ammonia on **o-nitro-mandelic nitrile** $NO_2[1]C_6H_4[2]CH(OH)CN$, with elimination of HCN (B. **39,** 2335). o-Nitroso-benzoic acid is also produced by the oxidation of phenyl-oxy-indol. **4-Nitro-** and **2, 4-dinitro-o-nitroso-benzoic acid** are transformation products of 2, 4-dinitro- and 2, 4, 6-trinitro-benz-aldehyde in light. **o-, m-,** and **p-nitroso-benzoic acid,** and their esters, are also obtained by the oxidation of the corresponding hydroxyl-amino-benzoic acids, which result from nitro-benzoic acids by reduction (B. **37,** 333).

5. **Hydroxylamino-carboxylic Acids.—o-Hydroxylamino-benzoic acid** $C_6H_4[2]NHOH[1]COOH$, brilliant needles, m.p. 142° with decomposition, obtained by reducing o-nitro-benzoic acid with zinc dust and sal ammoniac. It has the general properties of hydroxylamino-compounds: oxidising agents convert it into o-nitroso-benzoic acid, with

which it condenses in alkaline solutions to oo'-azoxy-benzoic acid. On warming with dilute H_2SO_4 it is partly transposed into 5-oxy-anthranilic acid $OH[5]C_6H_3[2]NH_2[1]CO_2H$, while the major part passes into its anhydride.

Benzisoxazolone, *oxy-anthranile*

$$\text{I. } C_6H_4\begin{cases}[1]CO\\[2]NH\end{cases}\!\!>O \quad \text{or} \quad \text{II. } C_6H_4\begin{cases}[1]C(OH)\\[2]N\text{---}\end{cases}\!\!>O,$$

m.p. 112° with decomposition. It has an acid character. While the alkali salts, on account of their very difficult breaking up into o-hydroxylamino-benzoic salts, must be regarded as probably derivatives of oxy-anthranile (formula II.), the alkyl- and acyl-benziso-oxazolones obtained from them are reducible to formula I., since, on reduction, they easily form N-alkyl- and acyl-anthranilic acids.

N-Acetyl-benzisoxazolone $C_6H_4\begin{cases}CO\\N(COCH_3)\end{cases}\!\!>O$, m.p. 118°, is also formed by condensation of o-nitroso-benzoic acid with paraldehyde under the influence of light (B. **42,** 2297).

6. **Aromatic Amido-monocarboxylic Acids.**—These are obtained by reducing the corresponding nitro-benzoic acids. Like glycocoll, the amido-benzoic acids yield crystalline salts both with acids and bases. They do not combine with acetic acid, hence are precipitated by it from their alkali salts.

Like glycocoll, these acids can be considered as cyclic ammonium salts (Vol. I.). The hydrogen atoms of the amido-group are replaceable by alkyl and acidyl residues. Dimethylated amido-acids are produced by the action of phosgene and aluminium chloride upon the dimethyl-anilines. Acetamido-benzoic acids are formed by the oxidation of the acetyl-toluidins.

The o-amido-acids (of which o-amido-benzoic acid and o-amido-phenyl-acetic acid are closely related to indigo, and o-amido-hydrocinnamic acid to quinolin) form hetero-rings, and yield rather remarkable ortho-condensation products.

Anthranilic acid, *o-amido-benzoic acid* $C_6H_4\begin{cases}[1]CO_2H\\[2]NH_2\end{cases}$ or $C_6H_4\begin{cases}[1]COO\\[2]NH_2\end{cases}$, m.p. 145°, sublimates at low pressures without decomposition (C. 1903, I. 922), but breaks down, upon heating, into aniline and carbonic acid. Its aqueous solution has a sweet taste; many of its organic solutions have a blue fluorescence (B. **31,** 1693) It was first obtained from *indigo* (*q.v.*) by the action of caustic potash (Fritzsche, 1841).

The oxidation can be accelerated by the addition of manganese dioxide (A. **234,** 146). The acid results from the reduction of o-nitro-benzoic acid and the two m-bromo-o-nitro-benzoic acids with tin and hydrochloric acid; from o-nitro-toluol by heating with concentrated potash (C. 1900, I. 1098), and from anthranile, acet-anthranilic acid, and isatoic anhydride by splitting. Cp. o-chloro-benzoic acid.

Industrially, it is obtained from phthalimide by treatment with bromine and caustic potash (B. **24,** R. 966; **36,** 218; *J. pr. Ch.* **2, 80,** 1):

$$C_6H_4(CO)_2NK+BrOK+2KOH = C_6H_4(NH_2)COOK+BrK+CO_3K_2.$$

It is also obtained from phthalic hydroxylamine with alkali (C. 1902, II. 1439).

Nitrous acid converts anthranilic acid, in aqueous solution, into salicylic acid, and sodium, in amyl-alcohol solution, into hexahydro-anthranilic acid, hexahydro-benzoic acid (*q.v.*), and n-pimelic acid (Vol. I.) (B. **27,** 2466).

With PCl_5 anthranilic acid forms chlorides: $COCl.C_6H_4NHPOCl_2$, m.p. 62°, and $(COCl.C_6H_4NH)_2POCl$, m.p. 148°–153° (B. **36,** 1824).

The **methyl ester,** m.p. 25·5°, b.p. 125°, is a characteristic constituent of *orange-blossom oil* and *neroli oil* (B. **32,** 1512), and is also found in the oil of flowers of *Tuberosa* (B. **36,** 1465). The *ethyl ether* boils at 260°. These esters are also obtained direct from phthalimide, in alcoholic alkaline solution, with alkali hypochlorite (C. 1903, I. 745). Also from isatoic anhydride, with sodium alcoholate and water (B. **33,** 28). Its *amide,* from isatoic acid and ammonia, melts at 108° (B. **18,** R. 273).

Unsym. phenyl-hydrazide, m.p. 134° (A. **301,** 89).

Anthranilic nitrile, *o-amido-benzo-nitrile, o-cyananiline* $NH_2[2]C_6H_4CN$, m.p. 49°, b.p. 267°, from nitro-benzo-nitrile, with $SnCl_2$ and HCl (B. **42,** 3711), or from o-amido-benzaldoxime by splitting off H_2O (B. **36,** 804); on heating with Am_2S it yields the **thiamide** $NH_2C_6H_4CSNH_2$, m.p. 122°; with HNO_2, *γ-amido-indazol* $C_6H_4\begin{cases}C(NH_2)\\NH\end{cases}\!\!>N$ (C. 1903, I. 1270; B. **42,** 3716).

Formyl-anthranilic acid $CHO.NH[2]C_6H_4[1]CO_2H$, melting at 169°, is produced in boiling isatoic acid with formic acid. It condenses on heating to **keto-dihydro-quinazolone-benzoic acid** $C_6H_4\begin{cases}CO.NC_6H_4COOH\\N=CH\end{cases}$ (B. **35,** 3475).

Acetyl-anthranilic acid $CH_3CO.NH[2]C_6H_4[1]CO_2H$ results from anthranilic acid treated with acetic anhydride; from o-aceto-toluidin, by oxidation with $KMnO_4$, in the presence of magnesium sulphate (B. **36,** 1801), and from the oxidation of methyl-ketol and of quinaldin (*q.v.*). The methyl ester, m.p. 61°, and the amide, m.p. 170°, have been obtained from anthranilic acid ester and amide. Heating of acetanthranilic acid, or its ester, with $POCl_3$ produces the so-called dianhydro-diacetanthranilic acid $C_{18}H_{14}N_2O_4$, m.p. 250°. By heating with acetic anhydride to 150°, or, by itself, to 200°–210°, acetanthranilic acid is partly anhydrated to acetanthranile, and partly condensed to **methyl-dihydro-quinazolone-benzoic acid** $C_6H_4\begin{cases}CO.NC_6H_4COOH\\N=CCH_3\end{cases}$ (B. **35,** 3470). **Benzoyl-anthranilic acid** $C_6H_5CONHC_6H_4COOH$, m.p. 183°, see B. **26,** 1304; A. **324,** 134. **Benzo-sulphone-anthranilic acid,** $C_6H_5SO_2NHC_6H_4COOH$, m.p. 214°; **chloride,** m.p. 155° (A. **367,** 104).

Anthranile $C_6H_4\begin{cases}CH\\|\\N\end{cases}\!\!>O$, b.p.$_{18}$ 99° (B. **42,** 1647), an oil of a peculiar odour, volatile in water vapour. It is dealt with in this place because it behaves, in many reactions, like an *anhydride of anthranilic acid,* $C_6H_4\begin{cases}CO\\|\\NH\end{cases}$ β-lactame, being transformed by alkalies into anthranilic acid, and by acetic anhydride into acetanthranile. These reactions, however, probably take place with an intramolecular atomic

displacement. A direct conversion of anthranilic acid into anthranile has not been hitherto accomplished. The modes of formation of anthranile are as follows: (1) from nitro-benzaldehyde by reduction with tin and acetic acid, or with ferrous sulphate and ammonia; (2) from acido-benzaldehyde; (3) from o-nitroso-benzyl alcohol, on boiling with water; (4) from amido-benzaldehyde by oxidation with Caro's acid. These reactions lead to the conclusion that anthranile is an anhydride or inner ether of the unstable o-hydroxylamino-benzaldehyde $C_6H_4\begin{cases}CHO\\NHO_{11}\end{cases}$ (see B. **36,** 3653), whose oxime is obtained by treating it with hydroxylamine, and whose nitroso-compound results from the action of HNO_2. This view is supported by the easy reduction of anthranile to o-amido-benzaldehyde, and the close relation to *anthroxanic acid* $C_6H_4\begin{cases}C—COOH\\|\quad\rangle O\\N\end{cases}$ (*q.v.*), apparent from the analogous formation and especially from the fact of its passing into anthranile on heating with water to 150° (*J. pr. Ch.* 2, **81,** 254). The improbability of the β-lactame formula is also seen by a comparison with dianthranilide, which must be taken as a true molecular anhydride of anthranilic acid. Anthranile is easily obtained from the dimercury compound of o-nitro-toluol by the action of concentrated HCl. With corrosive sublimate, anthranile forms a characteristic double compound $C_7H_5NO.HgCl_2$, m.p. 178°. With chlorine, it combines to form a *dichloride* $C_6H_4\begin{cases}CH\\|\quad\rangle O\\NCl_2\end{cases}$, m.p. 77°, which, on heating with water, passes into **B_2-monochlor-anthranile,** m.p. 79°, with migration of a chlorine atom B. **42,** 1701).

Methyl-anthranile $C_6H_4\begin{cases}C(CH_3)\rangle O\\N_____\end{cases}$, from o-nitro-aceto-phenone, and **phenyl-anthranile** $C_6H_4\begin{cases}C(C_6H_5)\rangle O\\N_____\end{cases}$, from o-nitro- or o-amido-benzo-phenone, must be regarded as true homologues of anthranile (B. **36,** 819, 2042). Anthranile derivatives are probably traceable in the compounds produced by the condensation of o-nitro-benzaldehyde with phenols and tertiary amines in the presence of concentrated HCl (B. **42,** 1714).

Acetyl-anthranile $C_6H_4\begin{cases}CO.O\\N=CCH_3\end{cases}$ or $C_6H_4\begin{cases}CO\\NCOCH_3\end{cases}$, m.p. 81°, b.p.$_{14}$ 147°, from anthranile or acetanthranilic acid, as well as carbox-ethyl-anthranilic acid, with acetic anhydride. It must therefore be regarded as a true anhydride of acetanthranilic acid. With NH_3 it yields o-acetamido-benzamide; with aniline and other amine bases it gives derivatives of methyl-dihydro-quinazolone $C_6H_4\begin{cases}CO.NR\\|\\N=CCH_3\end{cases}$. A similar behaviour is shown by **benzoyl-anthranile** $C_6H_4\begin{cases}CO.O\\N=CC_6H_5\end{cases}$ or $C_6H_4\begin{cases}CO\\NCOC_6H_5\end{cases}$, m.p. 122°, formed from benzoyl-anthranilic acid by splitting off H_2O; from anthranilic acid, benzoyl chloride, and pyridin in the cold; and from anthranile after several hours' heating with benzoyl chloride (B. **35,** 3480; **36,** 2766). The very smooth formation of acidyl-anthraniles from the acidyl-anthranilic acids, as well as the

close relations to the quinazolones, indicate the first formula rather than the second. This is corroborated by the anhydride formation of those acyl-anthranilic acids, like benzol-sulphone-anthranilic acid and picryl-anthranilic acid, in which the formation of compounds of the formula $C_6H_4\begin{cases}CO.O\\N=CR\end{cases}$ is difficult, or is impossible, dimolecular anhydrides being formed (see Dianthranilides, and A. **367,** 124). The acyl-anthraniles must therefore be regarded as β, γ-benzo-metoxazins, and are closely related to the anhydrides obtained from benzoyl-α-amido-acids; cp. hippuric acid, benzoyl-alalin, etc.

DIMOLECULAR ANHYDRIDES OF ANTHRANILIC ACID (A. **367,** 101).—While, therefore, anthranile cannot be regarded as a simple anhydride of anthranilic acid, dimolecular true anhydrides of anthranilic acid are known: anthranoyl-anthranilic acid, anthranoyl-anthranilic anhydride (anthranoyl-anthranile), and dianthranilide, which can all be broken up to obtain anthranilic acid.

Anthranoyl-anthranilic acid $NH_2[2]C_6H_4[1]COHN[2]C_6H_4[1]COOH$, m.p. 203°, is formed (1) by reduction of o-nitro-benzoyl-anthranilic acid; (2) by condensation of anthranilic acid with isatoic anhydride; and hence (3) as an intermediate product in the industrial preparation of anthranilic acid from phthalimide, sodium hypochlorite, and sodium hydrate (*J. pr. Ch.* 2, **80,** 1). On heating above the melting-point, or, more easily, by the action of thionyl chloride, it liberates water and passes into **anthranoyl-anthranilic-acid-O-anhydride,** *anthranoyl-anthranile* $C_6H_4\begin{cases}CO.O\\N=CC_6H_4NH_2\end{cases}$, m.p. 162°, yellow needles, easily polymerised on heating. Its *benzol-sulphone compound* $C_6H_4\begin{cases}CO.O\\N=C.C_6H_4NH.SO_2C_6H_5\end{cases}$, m.p. 223°, is formed by the action of benzol-sulpho-chloride upon anthranile (B. **40,** 997). By repeatedly treating anthranoyl-anthranilic acid with nitro-benzoyl chloride, and then reducing, anhydrides of anthranilic acid are obtained, which have a polypeptide character, *e.g.* $NH_2C_6H_4CO.NHC_6H_4CO.NHC_6H_4COOH$, etc. (A. **351,** 267).

Dianthranilide $C_6H_4\begin{cases}[1]NH.CO[2]\\[2]CO.NH[1]\end{cases}C_6H_4$, m.p. about 330°, colourless needles, is obtained from its monoacetyl compound, the product of the action of concentrated H_2SO_4 and glacial acetic acid upon dibenzol-sulphone-dianthranilide, on boiling with NaHO. It has the character of a weak dibasic acid, and yields a disodium salt, which, on methylation with dimethyl sulphate, passes into **N, N-dimethyl-dianthranilide** $C_6H_4\begin{cases}N(CH_3).CO\\CO\ (CH_3)N\end{cases}C_6H_4$.

Boiling with concentrated alkali breaks up the dianthranilide into two molecules of anthranilic acid.

Dibenzol-sulphone-dianthranilide $C_6H_4\begin{cases}N(SO_2C_6H_5)CO\\CO(SO_2C_6H_5)N\end{cases}C_6H_4$, m.p. 264°, is formed by heating benzol-sulpho-anthranilic chloride with pyridin.

Carboxyl-anthranilic dimethyl ester and **diethyl ester,** *isatoic dialkyl ester* $C_6H_4(NHCOOCH_3)COOCH_3$, m.p. 61°, b.p.$_{12}$ 166°, and m.p. 44°, b.p.$_{10}$ 174°, are obtained from phthalimide chloride, or bromide, $C_6H_4(CO)_2BrN$, by the action of sodium alcoholates; further action converts them into the acid isatoic esters: **carboxy-methyl** and **carboxy-**

ethyl-anthranilic acid $C_6H_4(NHCO_2C_2H_5)COOH$, m.p. 181° and 126°, also obtained from anthranilic acid with chloroformic esters, and from isatoic anhydride by heating with alcohols. Treatment with acetyl chloride converts them into **isatoic anhydride** $C_6H_4\begin{cases}CO.O\\NH.CO\end{cases}$, m.p. 233°–240°. It was first obtained by oxidising a glacial acetic acid solution of indigo with chromic acid (H. Kolbe, 1885), and, later, from anthranile and anthranilic acid by the action of chloro-carbonic esters (B. **22,** 1672). Also by conducting phosgene into sodium-anthranilate solution.

It is very sparingly soluble in water. Digested with alkalies or alkaline earths, it forms unstable salts of the formula $C_6H_4\begin{cases}CO.O\\N=COMe\end{cases}$, from which CO_2 regenerates isatoic anhydride. With excess of alkali, salts of isatoic acid are first formed, and these, digested with alkalies, or, instantly, on adding acids and CO_2, are broken up into CO_2 and anthranilic acid; free isatoic acid can therefore not be obtained (B. **32,** 2159; **33,** 21; *J. pr. Ch.* 2, **79,** 281). Ammonia, hydrazin, phenylhydrazin, and hydroxylamine change it into the corresponding amide derivatives of anthranilic acid (B. **19,** R. 65; **26,** R. 585).

Isatoic anhydride forms an important intermediate product in the industrial preparation of anthranilic acid from phthalimide, sodium hypochlorite, and NaHO, and can be isolated if an excess of NaHO is avoided. The processes involved are represented by the following system of formulæ (*J. pr. Ch.* 2, **80,** 1):

$$C_6H_4\begin{cases}CO\\CO\end{cases}NH \xrightarrow{NaOH} C_6H_4\begin{cases}COONa\\CONH_2\end{cases} \xrightarrow{ClONa} C_6H_4\begin{cases}COONa\\CON\begin{cases}Cl\\Na\end{cases}\end{cases} \xrightarrow{-NaCl}$$

$$C_6H_4\begin{cases}CO.O\\N=CONa\end{cases} \xrightarrow{NaOH} C_6H_4\begin{cases}COONa\\NHCOONa\end{cases} \xrightarrow{-CO_2} C_6H_4\begin{cases}COONa\\NH_2\end{cases}.$$

Kynuric acid, *oxalyl-anthranilic acid, carbostyrilic acid* $CO_2H.CONH[2]C_6H_4[1]CO_2H+H_2O$, becomes anhydrous at 100°, and melts at 180° with decomposition. It is formed from the quinolin derivatives—kynurin (*q.v.*), kynurenic acid (*q.v.*), α-phenyl-quinolin (*q.v.*), carbostyrile (*q.v.*), aceto-tetrahydro-quinolin, and indoxylic acid (*q.v.*)—by oxidation. It is prepared synthetically by heating anthranilic acid with oxalic acid to 130° (B. **17,** 401; R. 110). Its *monoethyl ester* $CO_2.C_2H_5CO.NH[2]C_6H_4[1]CO_2H$ is formed in the oxidation of the ester of indoxylic acid (B. **15,** 778). It melts at 180°.

Oxalyl-anthranilic acid nitrile, *o-cyano-anilic acid* $CO_2H.CONH[2]C_6H_4[1]CN$, m.p. 126°. The **methyl ester**, m.p. 139°, has been obtained by condensing o-amido-benzo-nitrile with oxalic ester. Dilute acids transpose the nitrile into the **isomeric 4-keto-dihydro-quinazolin-2-carboxylic acid** $C_6H_4\begin{cases}CO.NH\\N=C\end{cases}COOH$ (B. **42,** 3710).

Dicyanamino-benzoyl $C_6H_4\begin{cases}[1]CO.NH\\[2]N=C.CN\end{cases}$ (Anschütz) melts with decomposition. It results from cyanogen and o-amido-benzoic acid in aqueous solution (B. **11,** 1986). **Ethoxy-cyanamino-benzoyl** $C_6H_4\begin{cases}[1]CO.N\\\quad\|\\[2]NH.C.OC_2H_5\end{cases}$, melting at 173°, is formed from cyanogen and

anthranilic acid in alcoholic solution (B. **11,** 1986). Ammonia changes it to **o-benzo-glyco-cyamidin, benzoylene-guanidin** $C_6H_4\begin{cases}[1]CO.N \\ \| \\ [2]NH.C:NH\end{cases}$, which CH_3I, in strong alkaline solution, converts into **α-o-benzo-creatinin** $C_6H_4\begin{cases}[1]CO\text{———}N \\ \| \\ [2]N(CH_3)\text{—}C:NH\end{cases}$ (B. **18,** 977).

Methyl-anthranilic acid $CH_3NH[2]C_6H_4[1]COOH$, m.p. 182°, from anthranilic acid with soda and methyl iodide or dimethyl sulphate in methyl alcoholic, or aqueous, solution; also from o-chloro-benzoic acid with methyl-amine and copper (C. 1903, II. 1099). **Methyl ester** $CH_3NHC_6H_4COOCH_3$, b.p.$_{13}$ 129° (C. 1902, II. 1257). The acid is converted into indoxyl (and indigo) by heating with NH_2Na, alkali, or amalgams of alkaline earth metals; this conversion is even more direct in the case of the acyl-methyl-anthranilic acids: **formyl-methyl-anthranilic acid** $CHON(CH_3)C_6H_4COOH$, m.p. 169°, and **formyl-ethyl-anthranilic acid,** m.p. 119°, obtained from methyl- and ethyl-quinolinium salts by oxidation with permanganates (B. **36,** 1806; C. 1903, I. 745).

Nitroso-methyl-anthranilic acid $NO.N(CH_3)C_6H_4COOH$, m.p. 127°, from methyl-anthranilic acid with HNO_2 or oxidation of nitroso-methyl-o-toluidin with MnO_4K (B. **34,** 1644). Hydrochloric acid transposes it into **5-nitroso-methyl-anthranilic acid** $NO[5]C_6H_3[2]NHCH_3[1]COOH$, which, on boiling with soda solution, splits off methyl-amine, and passes into 5-nitroso-salicylic acid (B. **42,** 2745). On further methylation, methyl-anthranilic acid passes into **dimethyl-anthranilic acid** $(CH_3)_2N[2]C_6H_4[1]COOH$, m.p. 70°, from which **anthranilic betain,** *o-benzo-betaïn* $C_6H_4\begin{cases}N(CH_3)_2 \\ CO\text{———}\end{cases}\!\!>O$, m.p. 227°, is generated. The latter, on heating to 240°, transposes into **dimethyl-anthranilic methyl ester,** b.p.$_{11}$ 131° (B. **37,** 411; cp. m- and p-amido-benzoic acid, and anilido-acetic acid; also Betaïn, Vol. I.).

Ethyl-anthranilic acid, m.p. 153°, see B. **39,** 3236. **Diethyl-anthranilic acid,** m.p. 121°, M. **25,** 487.

Aryl-anthranilic acids are formed by heating o-chloro-benzoic acid with aromatic amines, in the presence of copper (A. **355,** 312). On heating alone, they split off CO_2, and pass into diphenyl-amines; and on heating with concentrated SO_4H_2, into acridone. **Phenyl-anthranilic acid** $C_6H_5NHC_6H_4COOH$, m.p. 181°, is also obtained by de-amidating amido-phenyl-anthranilic acid. **Diphenyl-anthranilic acid** $(C_6H_5)_2NC_6H_4COOH$, m.p. 208°, from phenyl-anthranilic acid, iodo-benzol, and copper. On heating, it decomposes into CO_2 and triphenyl-amine (B. **40,** 2448). **Picryl-anthranilic acid** $(NO_2)_3C_6H_2NHC_6H_4COOH$, m.p. 272° (A. **367,** 118). **Diphenyl-amine-o, o'-, -o, m'-** and **o, p'-dicarboxylic acid** $CO_2HC_6H_4NHC_6H_4CO_2H$, m.p. 295°, 296°, and 290° with decomposition, from o-chloro-benzoic acid with o-, m-, and p-amido-benzoic acid (A. **355,** 352). **Sym. diphenyl-p-phenylene-diamine-o, o'-dicarboxylic acid** $CO_2H[1]C_6H_4[2]NH[1]C_6H_4[4]NH[2]C_6H_4[1]CO_2H$, m.p. 288° with decomposition, from p-dibromo-benzol, anthranilic acid, and copper (C. 1906, II. 932).

Formaldehyde condenses with anthranilic acid in various molecular ratios, according to the conditions.

Methylene-dianthranilic acid, *formaldehyde-dianthranilic acid* CH_2

$(NH[2]C_6H_4COOH)_2$, m.p. 158° with decomposition, from 2 molecules anthranilic acid and 1 molecule formaldehyde solution, is transposed by methyl-alcoholic HCl into **p_2-diamido-diphenyl-methane-dicarboxylic acid** $CH_2[C_6H_3(NH_2)COOH]_2$; by acetylation with acetic anhydride and sodium acetate, we obtain **methylene-diaceto-anthranilic acid** $CH_2[N(COCH_3)C_6H_4COOH]_2$. Potassium cyanide splits up formaldehyde-dianthranilic acid into anthranilic acid and anthranilido-aceto-nitrile (A. **324**, 118). By the condensation of equimolecular quantities of formaldehyde and anthranilic acid, and its N-mono-substitution products ($CO_2HC_6H_4NHR$), we obtain compounds insoluble in alkalies, the so-called *formalides*, which may be used for characterising, and isolating, substituted anthranilic acids, since they are easily dissolved into their components on heating with acids or alkalies. **Anthranilic formalide** $C_6H_4\langle^{NH.CH_2}_{CO.O}$, m.p. 145°–148° with decomposition; **phenyl-anthranilic formalide** $C_6H_4\langle^{N(C_6H_5).CH_2}_{CO\text{——}O}$.

By treating with KCN or alkaline bisulphite, the formalides are split up, with formation of salts of ω-cyano-methyl-anthranilic acids $C_6H_4\langle^{NH.CH_2CN}_{COOH}$, and ω-sulpho-methyl-anthranilic acids $C_6H_4\langle^{NH.CH_2.O.SO_2H}_{COOH}$. With excess of formaldehyde, anthranilic acid combines, on heating, to form anthranilic diformalide; it forms a heavy yellow oil insoluble in alkali, combining with 1 molecule KCN to a *mononitrile* $C_6H_4\langle^{N(CH_2.CN).CH_2}_{CO\text{——}O}$, m.p. 105°, and with 2 molecules KCN to **anthranilido-diaceto-nitrile** $C_6H_4\langle^{N(CH_2CN)_2}_{COOH}$, m.p. 168°–171° with decomposition (B. **42**, 3534; C. 1910, I. 309). **Methylene-anthranilic acid** $CO_2HC_6H_4N:CH_2$, m.p. about 210° (B. **41**, 1565).

Anthranilido-acetic acid, *phenyl-glycin-o-carboxylic acid* $COOH[2]C_6H_4NHCH_2COOH$, m.p. 215° with decomposition, has acquired great technical importance on account of its transformation into *indoxyl* and *indigo*. It is formed: (1) from chloracetic acid and anthranilic acid, in neutral solution; with excess of chloracetic acid we obtain **anthranilido-diacetic acid** $COOHC_6H_4N(CH_2COOH)_2$, m.p. 212° with decomposition (B. **33**, 3182); (2) from anthranilic acid on heating with multivalent alcohols, like glycerine, mannite, etc. (C. 1900, II. 549); (3) by saponification of anthranilido-aceto-nitrile $COOH[2]C_6H_4NHCH_2CN$, m.p. 181° with decomposition, which is obtained from anthranilic acid, formaldehyde, and KCN, or by splitting up formaldehyde-dianthranilic acid, or anthranilic formalide with KCN (A. **324**, 118; *J. pr. Ch.* 2, **63**, 392; B. **39**, 989); (4) from o-chloro-benzoic acid, by heating with glycocoll in the presence of alkaline carbonate and copper (C. 1903, II. 81, 610). On heating with caustic alkalies, or acetic anhydride and sodium acetate, the acid passes into indoxyl and its derivatives, which are easily converted into *indigo*:

$$2C_6H_4\{^{NHCH_2CO_2H}_{COOH} \longrightarrow 2C_6H_4\{^{NH}_{C(OH)}\!\!>\!\!CCO_2H \xrightarrow[-2SO_2]{O} C_6H_4\{^{NH}_{CO}\!\!>\!\!C:C\!\!<\!\!^{NH}_{CO}\}C_6H_4.$$

The esters: **dimethyl ester,** m.p. 97°; **diethyl ester,** m.p. 75°, are condensed by means of sodium ethylate to *indoxylic acid esters*. The

condensation of anthranilido-acetic acid, and its esters, is facilitated by introducing acyl, or alkyl, groups into N-position.

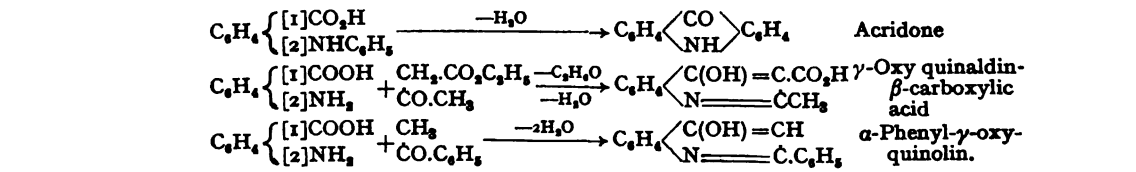
Acetanthranilido-acetic acid $COOHC_6H_4N(COCH_3)CH_2COOH$, m.p. 214° with decomposition; **diethyl ester,** m.p. 64°. **Methyl-anthranilido-acetic acid** $COOHC_6H_4N(CH_3)CH_2COOH$, m.p. 189° with decomposition (B. **35,** 1683; C. 1903, I. 305). **Phenyl-anthranilido-acetic acid** $COOHC_6H_4N(C_6H_5)CH_2COOH$, m.p. 166°; its nitrile is formed from phenyl-anthranilic formalide with KCN (C. 1910, I. 309).

p-Sulpho-anthranilic acid $SO_3H[4]NH_2[2]C_6H_3COOH$ is formed from o-nitro-toluol-sulphonic acid with NaHO, in a manner analogous to the formation of anthranilic acid from o-nitro-toluol (C. 1903, I. 371).

3, 5-Dibromo-anthranilic acid from o-nitro-toluol with bromine (M. **28,** 987). Of the six possible isomeric **dichloro-anthranilic acids,** five are known (B. **42,** 3533; C. 1910, I. 310). **Tetrachloro-anthranilic acid** $Cl_4C_6[2]NH_2[1]CO_2H$, m.p. 182°, from tetrachloro-phthalic anhydride (B. **42,** 3549). **5-Nitro-anthranilic acid** $NO_2[5]NH_2[2]C_6H_3CO_2H$, m.p. 269°, is obtained from its aceto-compound, m.p. 221°, which results from the oxidation of nitro-aceto-toluide with $(MnO_4)Ca$ (B. **36,** 1801); besides the isomeric acid $NO_2[4]NH_2[2]C_6H_3CO_2H$, it is formed from 4-nitro-phthalimide with KOBr (C. 1902, II. 359). In the same way, 3- and 6-nitro-anthranilic acids, m.p. 203° and 180° with decomposition, are formed from 3-nitro-phthalimide with KOBr. Dinitro-anthranilic acid $(NO_2)_2[3, 5]NH_2[2]C_6H_2COOH$, m.p. 265°, from dinitro-chloro-benzoic acid with NH_3 (C. 1901, II. 545).

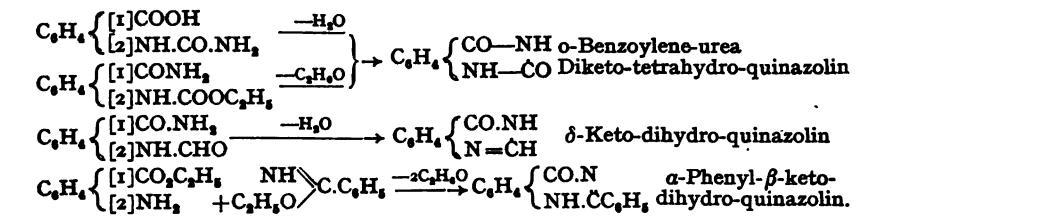
Hetero-ring Formations of Anthranilic Acid and its Derivatives.— It is evident from the formation of *acidyl anthraniles, isatoic anhydride, indoxyl,* and other substances mentioned above, that anthranilic acid and its derivatives are very prone to the formation of heterocyclic ring systems, and "ortho-condensation." (Compare o-amido-benzyl alcohol, o-amido-benzaldehyde, and o-amido-aceto-phenone.)

Acetyl-anthranilic acid and phenol condense, on heating, to *acridone,* which also results in digesting phenyl-anthranilic acid with concentrated sulphuric acid (B. **25,** 2740). Anthranilic acid condenses with aceto-phenone and aceto-acetic ester to *quinolin* derivatives (B. **27,** 1396):



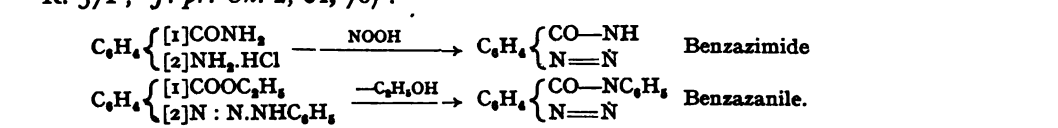
o-Benzoylene-urea is formed on heating anthranilic acid and anthranil-amide with urea. It also results upon heating carboxethyl-o-amido-benzamide (B. **2,** 416; **22,** R. 196), as well as by the action of mineral acids upon uramido-benzoic acid (B. **27,** 976). *Keto-dihydro-quinazolins* are produced on heating formyl-, acetyl-, and benzoyl-o-amido-benzamide. The β-methyl compound is formed in the action of acetamide upon anthranilic acid, and ammonia upon ethyl-acetamido-benzoic ester (B. **20,** R. 630; **22,** R. 196; **27,** R. 516; C. 1903, I. 174, 1270). α-Phenyl-β-keto-dihydro-quinazolin results from heating anthranilic-acid ester with benzimido-ethyl ester (C. 1906, II. 1124).

The condensation products of o-amido-benzoic acid and cyanogen gas have been described and formulated :



Nitrous acid converts anthranil-amide directly into benzazimide, whereas the o-diazo-benzoic ester first resulting from anthranilic ester must be treated with ammonia to effect this change. Similarly, anthranilic thio-amide gives rise to *thio-benzazimide* (B. **42,** 3719).

o-Diazo-amido-benzol-carboxylic ester, m.p. 76°, on boiling with alcohol, gives **α-phenyl-pheno-β-triazone** or **benzazanile** (B. **21,** 1538, R. 571 ; *J. pr. Ch.* 2, **64,** 70) :



m- and **p-Amido-benzoic acid** melt at 173° and 186° respectively. Their aceto-compounds, melting at 250° and 256°, result when m- and p-aceto-toluide are oxidised by permanganates (B. **36,** 1801) ; **p-amino-benzo-nitrile,** m.p. 86° (see C. 1903, II. 113). **m-Amino-benzo-nitrile,** m.p. 53° (see C. 1904, II. 100). **m-** and **p-Methyl-amido-benzoic acid** $CH_3NHC_6H_4CO_2H$, m.p. 127° and 161°, are produced by methylating the amido-acids with dimethyl sulphate (B. **43,** 210 ; **42,** 3744). The p-methyl-amido-benzoic acid is obtained, by nuclear synthesis, from the magnesium-iodide compound of methyl-aniline $C_6H_5N(CH_3)MgI$, by the action of CO_2 and transposition of the first product, a *carbaminate* $C_6H_5N(CH_3)COOMgI$, by heating, in a process akin to the synthesis of salicylic acid. From N-methyl- and ethyl-o-toluidin, in a similar manner, **p-methyl-amido-** and **p-ethyl-amido-m-methyl-benzoic acids** are generated, melting at 201° and 170° respectively. Dimethyl-aniline and diethyl-aniline react similarly with CH_3MgI and CO_2, forming **p-dimethyl-** and **p-diethyl-amido-benzoic acid,** m.p. 236° and 193° (B. **42,** 4488, 4815).

By methylation with ICH_3 and KOH, m- and p-amido-benzoic acids, like anthranilic acid, yield compounds resembling betaïn $C_6H_4\begin{cases}N(CH_3)_2\\CO\end{cases}O$, which, on heating, isomerise to m- and p-dimethyl-amido-benzoic ester (B. **37,** 414). **p-Amido-benzoic-diethyl-amino-ethyl ester** $NH_2[4]C_6H_4[1]COOCH_2CH_2N(C_2H_5)_2+2H_2O$, m.p. 51°, melting at 61° when anhydrous, results from the interaction of p-nitro-benzoyl chloride and ethylene chloro-hydrin, followed by reduction and transformation with diethyl-amine. Its monochloro-hydrate, m.p. 156°, is used as a local anæsthetic under the name of Novocaïn (A. **371,** 125).

Chrysanisic acid, 3, 5-dinitro-4-amido-benzoic acid $(NO_2)_2(NH_2)$.

$C_6H_2CO_2H$, melting at 259°, consists of golden-yellow flakes, and is produced when 3, 5-dinitro-4-methoxy-benzoic acid is heated with aqueous ammonia.

Diamido-benzoic acids $(NH_2)_2C_6H_3CO_2H$ are prepared by reducing the dinitro- and the nitro-amido-benzoic acids. **2, 4-Diamido-benzoic acid** $(NH_2)_2[2, 4]C_6H_3COOH$ is obtained from its diaceto-compound (B. **36,** 1803). The acids break down in dry distillation into carbon dioxide and phenylene-diamines. Like the o-phenylene-diamines, the diamido-benzoic acids, containing two amido-groups in the ortho-position with reference to each other, readily yield heterocyclic derivatives—*e.g.* nitrous acid converts 3, 4-diamido-benzoic acid into 3, 4-*azimido-benzoic acid* (B. **15,** 1880). The m, p- and the p, m-amido-uramido-benzoic acids yield two different uramido-azimido-benzoic acids, which afford the same azimido-benzoic acid by saponification (B. **29,** R. 586). The 2, 3-diamido-benzoic acid forms characteristic compounds, with many varieties of sugar.

3, 4, 5-Triamido-benzoic acid $(NH_2)_3.C_6H_2.CO_2H$, from chrysanisic acid by reduction, breaks down, when heated, into CO_2 and 1, 2, 3-triamido-benzol (A. **163,** 12). **2, 3, 5-Triamido-benzoic acid** (B. **15,** 2199), from dinitro-anthranilic acid (C. 1902, II. 1293).

Many amido-acids, derived from alkyl-benzoic acids, are known; also haloid amido-acids, nitro-amido-acids, etc.

Amido-phenyl-fatty acids are obtained from the nitro-phenyl-fatty acids. Certain o-amido-phenyl-fatty acids are particularly noteworthy because of their tendency to form inner anhydrides: γ- or δ-*lactames* (I. 359), which is so great that the corresponding free o-amido-acids are not capable of existing—*e.g.* o-amido-phenyl-acetic acid and o-amido-phenyl-hydro-cinnamic acid.

m- and *p-Amido-phenyl-acetic acids* melt at 149° and 200°.

m- and *p-Amido-hydro-cinnamic acids* „ 84° „ 131°.

4-*Amido*-3-*nitro-hydro-cinnamic acid*, from p-acetamido-hydro-cinnamic acid, melts at 145°.

p-Amido-hydratropic acid, melting at 128°.

γ- and δ-Lactames of the o-Amido-phenyl-fatty Acids.—Oxindol, *the lactame of o-amido-phenyl-acetic acid*, $C_6H_4\begin{cases}[1]CH_2.CO\\[2]NH\end{cases}$, melting at 120°, is obtained by the reduction of o-nitro-phenyl-acetic acid with tin and hydrochloric acid, and from dioxindol with sodium amalgam. If heated to 150° with baryta water it is converted into the barium salt of o-amido-phenyl-acetic acid, from which oxindol is separated by acids (B. **16,** 1704). Nitrous acid converts it into isatoxime (*q.v.*).

Oxindol boiled with acetic anhydride yields **aceto-oxindol,** $C_6H_4\begin{cases}[1]CH_2.CO\\[2]N<CO.CH_3\end{cases}$, melting at 126°. It dissolves to **aceto-o-amido-phenyl-acetic acid** $CH_3.CO.NH.C_6H_4.CH_2.CO_2H$, melting at 142°. Heated with alkalies or acids it breaks down into oxindol and acetic acid.

p-Amido-oxindol $NH_2.C_8H_6NO$, melting about 200°, is formed by the reduction of 2, 4-dinitro-phenyl-acetic acid with tin and hydrochloric acid. If ammonium sulphide be used as the reducing agent, the product will be 4-*amido*-2-*nitro-phenyl-acetic acid*, melting at 185° (B. **14,** 824); compare o-nitro-phenyl-iso-nitroso-acetic acid.

Atroxindol, *lactame of o-amido-hydratropic acid,* $C_6H_4\{^{[1]CH(CH_3).CO}_{[2]NH}$, melts at 119°.

Hydrocarbo-styrile, *lactame of amido-hydro-cinnamic acid,* melting at 163°, is formed by the reduction of o-nitro-hydro-cinnamic acid with tin and hydrochloric acid (Glaser and Buchanan, 1869) (B. **15,** 2103); by heating hydrocarbo-styrile-carboxylic acid, resulting from the reduction of o-nitro-benzyl-malonic acid (B. **29,** 667); and from hydrindone oxime by Beckmann's transposition (B. **29,** 667).

Hydrocarbo-styrile has the same relation to quinolin that oxindol bears to indol:

$C_6H_4\{^{[1]CH_2.CH_2}_{[2]NH.CO}$ Hydrocarbo-styrile $C_6H_4\{^{[1]CH=CH}_{[2]N=CH}$ Quinolin.

p-Amido-hydrocarbo-styrile $NH_2C_9H_8NO$, m.p. 211°, is formed, together with 4-amido-2-nitro-hydro-cinnamic acid, melting at 139°, from 2, 4-dinitro-hydro-cinnamic acid.

7. **Diazo-benzoic Acids** are produced from the mineral acid salts of the amido-benzoic acids with nitrous acid, just as the ordinary diazo-bodies are obtained from the aniline salts. Nitrous acid converts the amide of o-amido-benzoic acid into **benzazimide.** The free diazo-benzoic acids are very unstable. The **diazide** of **anthranilic acid** $C_6H_4\{^{[1]CO}_{[2]N_2}\rangle O$ consists of white, glistening needles. It is obtained when the chloride is acted upon with silver oxide (B. **29,** 1535).

8. **Diazo-amido-benzoic Acids** are formed when nitrous acid is conducted into the alcoholic solution of the amido-benzoic acids. **Diazo-m-amido-benzoic acid** $CO_2H[1]C_6H_4[3]N=N-NH[3']C_6H_4[1']CO_2H$ is an orange-red powder. Hydrofluoric acid converts it into m-fluoro-benzoic acid.

9. **Diazo-imido-benzoic Acids** $\begin{matrix}N\\ \|\\ N\end{matrix}\rangle N.C_6H_4CO_2H$ result when ammonia acts upon the perbromides of diazo-benzoic acids, or when hydrazin-benzoic acids are treated with nitrous acid. The o-body melts at about 70°; the *meta-* at 160°; and the p-compound at 185° (B. **9,** 1658).

10. **Azoxy-benzoic Acids** $O\langle\begin{matrix}N.C_6H_4CO_2H\\ |\\ N.C_6H_4CO_2H\end{matrix}$ are formed in the reduction of the nitro-benzoic acids with alcoholic potash. The o-derivative is also produced when n-oxy-indol-carboxylic acid (*q.v.*) is oxidised with alkaline potassium permanganate (B. **17,** 1904; **24,** R. 666; **29,** 656).

11. **Azo-benzoic Acids** $\begin{matrix}N.C_6H_4.CO_2H\\ |\\ N.C_6H_4.CO_2H\end{matrix}$. These result from the action of sodium amalgam upon the nitro-benzoic acids; or from the action of zinc dust and NaHO in alcoholic solution upon the same; or from the action of highly concentrated NaHO upon nitro-benzaldehydes (B. **34,** 4132; C. 1904, I. 722). o-, m-, and p-Azo-benzoic acid decompose on melting. By the distillation of the calcium salts, azo-phenylene, or phenazin, is formed.

Azo-benzol-o-monocarboxylic acid $C_6H_5N_2[1]C_6H_4[2]COOH$, m.p. 92°, and its homologues, result from the condensation of o-nitro-benzoic acid with primary anilines (C. 1909, I. 69). PCl_5 converts

them into *γ-oxy-β-phenyl-indazols* (*q.v.*) (C. 1907, I. 469). **Azo-benzol-m-monocarboxylic acid,** m.p. 171°. **Azo-benzol-p-monocarboxylic acid** $C_6H_5N_2C_6H_4$[4]COOH, m.p. 238°, is obtained from p-amido-azo-benzol, by way of the cyanide, and from benzol-azo-p-toluol by oxidation with chromic acid (A. **303,** 385).

o-Tolyl-azo-benzoic acid CH_3[2]$C_6H_4N : NC_6H_4$[2]COOH, m.p. 148°, from o-nitro-toluol by the action of finely divided metals and alkaline hydrate (C. 1903, II. 973). **m-** and **p-Benzaldehyde-azo-m-** and **-p-benzoic acid** $CHOC_6H_4N_2C_6H_4COOH$ is formed from m- and p-azoxy-benzaldehyde by transposition with concentrated H_2SO_4 (B. **36,** 3469, 3801).

12. **Hydrazin-benzoic Acids.**—The symmetrical hydrazo-benzoic acids result when the azo-benzoic acids are reduced with sodium amalgam, or with ferrous sulphate and sodium hydroxide. **o-Hydrazo-benzoic acid** melts at 205°. **m-Hydrazo-benzoic acid** CO_2H[3]C_6H_4[1]NH.NH[1′]C_6H_4[3′]CO_2H. These two acids, when boiled with hydrochloric acid, rearrange themselves to diamido-diphenyl-dicarboxylic acids (*q.v.*). The rearrangement of the m-acid into p-diamido-diphenic acid is of importance for the proof of the constitution of diphenic acid (*q.v.*), and consequently that of phenanthrene. **p-Hydrazo-benzol-carboxylic acid** $C_6H_5NHNHC_6H_4$[4]COOH, m.p. 193°, on transposition gives benzidin, with liberation of CO_2 (A. **303,** 384).

o-, m- and **p-Hydrazin-benzoic acids** $NH_2.NH.C_6H_4.CO_2H$ result when the hydrochlorides or nitrates of diazo-benzoic acids are reduced.

o-Cyano-phényl-hydrazin NH_2NH[2]C_6H_4CN, m.p. 153°, from o-diazo-benzo-nitrile by reduction, seems also to be formed by the reduction of the pheno-β-triazone oxime $C_6H_4\begin{cases}C(NOH).NH\\N=\!=\!=N\end{cases}$ (B. **36,** 805).

o-, m-, p-Benzoic-thionyl-hydrazone $SO : NNHC_6H_4COOH$, m.p. 155°, 231°, 258° (B. **27,** 2555). **Benzylidene-o-hydrazin-benzoic acid** $C_6H_5CH : NNH.C_6H_4COOH$, m.p. 224°, is reduced by sodium amalgam to o-benzyl-hydrazin-benzoic acid $C_6H_5CH_2NHNHC_6H_4COOH$, m.p. 134° with decomposition. On heating alone, or, better, with $POCl_3$ in an open vessel, o-hydrazin-benzoic acid yields an inner anhydride, **o-hydrazin-benzoic lactazame** $C_6H_4\begin{cases}CO\\NH\end{cases}\!\!>NH$, m.p. 242° with decomposition; while, on heating with $POCl_3$ under pressure, **chlorindazol** $C_6H_4\begin{cases}CCl\\|\\N\end{cases}\!\!>NH$ is formed (B. **35,** 2315).

13. **Phosphine-benzoic Acids.** — *Trimethyl-phospho-p-benzo-betaïn* $C_6H_4\begin{cases}[1]CO\!-\!\!-\!\!-\\[4]P(CH_3)_3\end{cases}\!\!>O$ is obtained from p-tolyl-trimethyl-phosphonium chloride by oxidation with alkaline permanganate; similarly, the trimethyl-phospho-tolu-betaïn is formed from trimethyl-xylyl-phosphonium chloride (B. **31,** 2919).

14. **Sulpho-benzoic Acids.**—On conducting the vapours of SO_3 into benzoic acid, we obtain as chief product *m-sulpho-benzoic acid,* and in smaller amount *p-sulpho-benzoic acid* (A. **178,** 279).

The three isomerides can be obtained by oxidising the three toluol-sulphonic acids with an alkaline solution of potassium permanganate.

If the toluol sulphamides, instead of the free acids, be subjected to similar oxidation, the m- and p-toluol sulphamides yield m- and p-sulph-

amine-benzoic acids; whereas the o-toluol sulphamide changes to benzoic sulphinide, or anhydro-sulphamine-benzoic acid, called *saccharin* (B. **12,** 469), from which, by saponification with HCl, the o-sulpho-benzoic acid is obtained (B. **33,** 3485). o- and p-sulpho-benzoic acid are formed together on boiling potassium-m-nitro-benzol sulphonate with an aqueous solution of KI; as in the formation of chloro-benzoic acids from halogen nitro-benzols with KCN, the entering cyanogen group does not take the place of the expelled nitro-group (C. 1905, II. 230).

o-Sulpho-benzoic acid $SO_3H[2]C_6H_4CO_2H+3H_2O$, m.p. 141° (anhydrous) behaves somewhat like phthalic acid (*q.v.*). It forms, for instance, *phthaleïns* (*q.v.*) (C. 1898, II. 717, 1105), an anhydride, and an imide. By the action of PCl_5 two dichlorides are obtained, m.p. 40° and 79°, the more stable one with the higher melting-point being probably represented by the formula $C_6H_4\{^{COCl}_{SO_2Cl}$, and the other by the formula $C_6H_4\{^{CCl_2}_{SO_2}\rangle O$. On boiling with alcohols they yield ester-sulphonic acids $SO_3HC_6H_4COOR$; with sodium ethylate, o-sulpho-benzoic-diethyl ester, b.p.$_{22}$ 212°; with ammonia, the sym. chloride (m.p. 79°) gives benzoyl sulphinide, while the unsym. unstable chloride gives chiefly **o-cyano-benzol-sulphonic acid** $CN[1]C_6H_4[2]SO_3H$, m.p. 279° (chloride, m.p. 67·5°), which has also been obtained from o-aniline-sulphonic acid by way of the diazo-compound (B. **28,** R. 751). With aniline the chlorides form **o-sulpho-benzoic anile** $C_6H_4\langle^{SO_2}_{CO}\rangle NC_6H_5$, m.p. 190°, **sym. dianilide** $C_6H_4(CONHC_6H_5)SO_2NHC_6H_5$, m.p. 195°, and **unsym. dianilide** $C_6H_4\langle^{C(NHC_6H_5)_2}_{SO_2}\rangle O$, m.p. 270°–280° with decomposition; while, with $POCl_3$, the two last give the **dianile** $C_6H_4\langle^{C(:NC_6H_5)}_{SO_2}\rangle NC_6H_5$, m.p. 189°.

On reduction the unstable chloride gives sulpho-benzide, and the stable chloride gives **thio-salicylic acid** $SH.C_6H_4COOH$. Condensation with benzene and Al_2Cl_6 gives mainly the *sym.* product $C_6H_5COC_6H_4SO_2C_6H_5$. The *unsym.* triphenyl-methane derivative is also obtained, $(C_6H_5)_2C.C_6H_4SO_2O$ (B. **31,** 1648; C. 1906, II. 329). p-Nitro- and p-bromo-o-sulpho-benzoic acids, with PCl_5, also give two isomeric dichlorides each, which are transformed in a similar manner (C. 1904, I. 274, 369).

o-Sulpho-benzoic anhydride, m.p. 118°, from the acid with acetyl chloride. With benzene and Al chloride it yields **benzo-phenone-o-sulphonic acid** $C_6H_5CO.C_6H_4SO_3H$ (B. **33,** 3486); the isomeric **phenyl-sulphone-o-benzoic acid** $C_6H_5.SO_2.C_6H_4COOH$, m.p. 268°, is formed from phenyl-o-tolyl sulphone by oxidation (C. 1901, I. 692).

o-Sulpho-chloride-benzoic methyl ester $SO_2Cl.C_6H_4COOCH_3$, m.p. 65°, from o-benzo-sulphinic-acid ester $SO_2H.C_6H_4COOCH_3$, m.p. 99°, treated with chlorine. This ester is prepared from anthranilic acid ester by diazotating, and replacing the diazo-group by the sulphinic residue (C. 1901, II. 961).

o-Sulphamido-benzoic acid $NH_2SO_2[2]C_6H_4[1]COOH$ melts at 153°–155°, with transition into the sulphinide. Methyl and ethyl

ester, m.p. 119° and 84° respectively (C. 1899, I. 1093). The acid is formed by the oxidation of o-toluol-sulphamide with red prussiate of potash (B. **19,** R. 689), and from its inner anhydride with warm alkaline hydrate. On fusing sulpho-benzoic acid with ammonium sulpho-cyanide the isomeric **o-benzamido-sulphonic acid** is formed, $C_6H_4(CONH_2)SO_3H$, m.p. 194°, which, with potassium hypobromite, yields o-sulphanilic acid (B. **29,** R. 102).

o - Anhydro - sulphamine - benzoic acid, *benzoic sulphinide* $C_6H_4\begin{cases}[1]CO\\[2]SO_2\end{cases}NH$, called **saccharin,** melts at 220°. It was discovered in 1879 by Ira Remsen and C. Fahlberg. Its preparation is given above. This compound is now made technically in very large quantities. It is used for sweetening purposes. It is 500 times sweeter than cane sugar. It dissolves with difficulty in cold water, and, like succinimide and phthalimide, behaves like a strong acid, forming imide salts. The sodium salt $C_6H_4\begin{cases}[1]CO\\[2]SO_2\end{cases}NNa$ is very readily soluble in water, and is 400 times sweeter than cane sugar. It is readily transposed by such haloid derivatives as benzyl chloride and acetyl chloride to N-derivatives of saccharin (B. **25,** 1737; **29,** 1048).

o-Sulpho-benzoic anile $C_6H_4\begin{cases}SO_3\\CO\end{cases}N.C_6H_5$, melting at 190°, results from the action of aniline upon the chlorides of sulpho-benzoic acid (B. **29,** R. 353). Phosphorus pentachloride converts saccharin into **pseudo-saccharin chloride** $C_6H_4\begin{cases}[1]CCl\\[2]SO_2\end{cases}N$, melting at 149° (B. **29,** 2995). At 70°–75° o-cyano-benzol-sulpho-chloride is formed (B. **29,** 2295; C. 1906, I. 1609). With phenols and amido-phenols saccharin condenses to dyes of the phthaleïn type, called saccharеïns (C. 1897, II. 847; 1899, I. 718).

All sulpho-acids containing the sulpho-group in the o-position with reference to the carboxyl group of an alkyl-benzoic acid are capable of forming *sulphinides* or *sulpho-carbonimides* (B. **25,** 1737).

On esters and ester acids from o- and p-sulpho-benzoic acid, see M. **23,** 1093.

3, 5-Disulpho-benzoic acid is formed by heating benzoic acid with fuming sulphuric acid containing 70 per cent. SO_3 to 250° in a pressure tube (B. **35,** 2305). **2, 4-Disulpho-benzoic acid,** from 2, 4-toluol-disulphonic acid (B. **14,** 1205).

Diphenyl-sulphone-o-monocarboxylic acid $C_6H_5SO_2[2]C_6H_4[1]COOH$, m.p. 144°, is formed by oxidation of phenyl-o-tolyl-sulphone and phenyl-thio-salicylic acid with $KMnO_4$, or by heating the potassium salts of o-chloro-benzoic acid and benzol-sulphinic acid in aqueous or amyl-alcoholic solution, in the presence of copper. On heating with concentrated H_2SO_4 the acid passes into **benzo-phenone-sulphone** $C_6H_4\begin{cases}SO_2\\CO\end{cases}C_6H_4$ (B. **38,** 729; C. 1905, I. 1394).

(*d*) Monohydric Oxy-phenyl-paraffin Alcohols and their Oxidation Products.

1. **Monohydric Oxy-phenyl-paraffin Alcohols, or Phenol Alcohols.** —These alcohols contain, in addition to the alcoholic hydroxyl, other hydroxyl groups joined to the benzene nucleus, which impart to them

the character of phenols. Some of the alcohols of this group are simple transposition products of long-known plant-substances. Special interest attaches to a number of mono- and dioxy-phenyl-ethyl-amines on account of their strong physiological action, and their occurrence in animals and plants ; cp. p-oxy-phenyl-ethyl-amine and hordenin.

Formation.—Some of the methods described under the benzyl alcohols also lead to phenol alcohols :

(1) The reduction of corresponding aldehydes and ketones.

(2) The treatment of aldehydes with caustic alkali.

(3) The action of sodium amalgam upon amides (B. **24,** 175).

(4) They are linked to the benzyl alcohols through the amido-phenyl-paraffin alcohols, which nitrous acid converts into oxy-phenyl-paraffin alcohols.

(5) *Nuclear Synthesis.*—Methylene chlorides (B. **13,** 435) or formaldehyde and sodium hydroxide (B. **27,** 2411 ; **35,** 3844 ; **40,** 2524 ; *J. pr. Ch.* 2, **50,** 225) change phenols into phenyl alcohols. Phenols with so-called " negative " substituents (NO_2, Cl, CHO, COOH) condense with formaldehyde and HCl to oxy-benzyl chlorides, in which the chlorine atom is very easily replaced by OH or OR (B. **34,** 2455 ; C. 1902, II. 894) ; (6) by the action of alkyl-magnesium haloids upon phenol-carboxylic ester. Closely related to formation (5) of the phenyl alcohols is the nuclear-synthetic formation of acylated oxy-benzyl-amines by the condensation of phenols with N-methylol-acyl-amides $RCONHCH_2OH$ (A. **343,** 215).

Monoxy-benzyl Alcohols $HOC_6H_4.CH_2OH$.—The three theoretically possible isomerides have been prepared. They result when the corresponding aldehydes are reduced with sodium amalgam. *Saligenin,* or o-oxy-benzyl alcohol, is the best-known member of the group :

o-Oxy-benzyl alcohol . . .	m.p. 82°
m-Oxy-benzyl alcohol . . .	,, 67°
p-Oxy-benzyl alcohol . . .	,, 110°.

Saligenin, or *o-oxy-benzyl alcohol,* was first obtained in the decomposition of the glucoside *salicin* (*q.v.*) by means of *emulsin, ptyalin,* or dilute acids (Piria, 1845 ; A. **56,** 37) :

$$C_6H_{11}O_5.O.C_6H_4.CH_2OH + H_2O = HO.C_6H_4CH_2OH + C_6H_{12}O_6.$$

Saligenin has also been prepared by the usual methods, from *salicyl-aldehyde, salicyl-amide, o-amido-benzyl alcohol,* and *phenol.* It is soluble in hot water, alcohol, and ether. Ferric chloride produces a deep-blue colour in its solutions. Acids resinify it, forming *salinetin* (*ῥητίνη,* resin). Ethers and substitution products of saligenin are known. These have been made in part from the corresponding salicyl derivatives.

o-Oxy-benzyl-amine, *salicyl-amine,* melts at 121° (B. **23,** 2744). **o-Oxy-benzyl-aniline,** m.p. 108°, is also obtained by combining anhydro-formaldehyde-aniline with phenol (C. 1900, II. 457 ; A. **315,** 138). The O-acetyl compounds of o-oxy-benzyl-amines and -anilines are unstable, and transpose spontaneously into the isomeric N-acetyl compounds (A. **332,** 159). Steric resistances are encountered in the acetylation of substituted o-oxy-benzyl-anilines (B. **32,** 2057).

Anisyl alcohol, *p-methoxy-benzyl alcohol* $CH_3O[4]C_6H_4[1].CH_2.OH$, is obtained from anisic aldehyde by alcoholic potassium hydroxide. It melts at 45°, and boils at 259°. It forms anisic aldehyde when oxidised.

p-Homo-saligenin $CH_3[5]C_6H_3[2](OH)CH_2.OH$ melts at 105°, from p-cresol by method 5 (B. **42,** 2539).

p-Thymotin alcohol $CH_3[2]C_3H_7[5]C_6H_2[4]OH[1]CH_2OH$, m.p. 120° (B. **27,** 2412).

o-Oxy-phenyl-ethyl alcohol $HO[2]C_6H_4[1]CH_2CH_2OH$, b.p. 169°, is formed by the splitting up of *cumarone* $C_6H_4\begin{cases}[1]CH:CH\\[2]O\text{——}\end{cases}$ (*q.v.*) with alcoholic potash, besides oxy-phenyl-acetic acid; the bromide of the alcohol, on treatment with NaHO, gives the cyclic phenol-alcohol ether, the so-called hydro-cumarone $C_6H_4\begin{cases}[1]CH_2CH_2\\[2]O\text{——}\end{cases}$, m.p. 188°, also formed from cumarone by reduction with Na and alcohol, and from bromo-methyl-o-bromo-phenyl ether $BrC_6H_4OCH_2.CH_2Br$ by condensation with sodium. **o-Oxy-phenyl-ethyl-amine** $HO[2]C_6H_4[1]CH_2CH_2NH_2$, with a chlorohydrate of m.p. 153°, is formed from the hydrazide of melilotic acid by disintegration. The quaternary iodo-methylate of the base, obtainable by the action of ICH_3, melts at 218°. On heating with NaHO it splits off trimethyl-amine and yields hydro-cumarone (B. **38,** 2067). **p-Oxy-phenyl-ethyl-amine** $HO[4]C_6H_4[1]CH_2CH_2NH_2$, m.p. 162°, increases the blood-pressure, like the closely related adrenalin (*q.v.*). It is formed from tyrosin (*q.v.*), an important product of the decomposition of albumin, by further decomposition, or by heating with rejection of CO_2. Synthetically, the p-oxy-phenyl-ethyl-amine is obtained by reduction of oxy-benzyl cyanide, or from the anisylidene-nitro-methane $CH_3O[4]C_6H_4[1]CH:CHNO_2$ by reduction and saponification with HI (B. **42,** 4778). By methylation of p-methoxy-phenyl-ethyl-amine and saponification of the methoxyl group with HI, we obtain **p-oxy-phenyl-dimethyl-ethyl-amine,** *hordenin* $HO[4]C_6H_4[1]CH_2CH_2N(CH_3)_2$, m.p. 117°, an alkaloid forming the effective ingredient of barley seeds (B. **43,** 306).

p-Oxy-phenyl-iso-propyl-amine $HOC_6H_4CH_2.CH(NH_2)CH_3$, m.p. 126°, by reduction of p-oxy-phenyl-acetoxime (B. **43,** 192).

o-Oxy-phenyl-ethyl-carbinol $HO[2]C_6H_4CH(OH)C_2H_5$, b.p.$_{0\cdot25}$ 125°–130°, by reduction of o-oxy-phenyl-ethyl ketone, and synthetically from tetra-acetyl-helicin with zinc ethyl (C. 1902, II. 214; B. **36,** 2575).

o-Oxy-phenyl-diethyl-carbinol $HO[2]C_6H_4C(OH)(C_2H_5)_2$, m.p. 57°, from salicylic ester, with C_2H_5MgI. It easily splits off water, and passes into olefin-phenol (C. 1903, I. 1222).

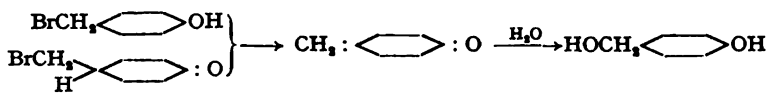
o-Chloro-p-oxy-benzyl alcohol and **p-chloro-o-oxy-benzyl alcohol** $ClC_6H_3(OH)CH_2OH$; also **o-nitro-p-oxy-** and **p-nitro-o-oxy-benzyl alcohol,** are produced in the form of their easily saponified haloid esters (see Pseudo-phenol haloids) from chloro- and nitro-phenols with formaldehyde and halogen hydride. The **p-amido-saligenin** $NH_2[4]C_6H_3[2]OH[1]CH_2OH$, formed by reduction of p-nitro-o-oxy-benzyl alcohol, is used as a photographic developer, under the name " edinol " (B. **34,** 2455; C. 1902, II. 394, 1439).

PSEUDO-PHENOL HALOIDS, METHYLENE-QUINONES, QUINOLS.

Pseudo-phenol Alcohol Haloids.—A peculiar behaviour is shown by certain halogen-hydrogen esters of phenol alcohols, especially those o- and p-oxy-benzyl bromides and chlorides in which nuclear H atoms are replaced by chlorine or bromine. Such products are obtained (1) by the action of HBr upon the corresponding phenol alcohols; (2) from vinyl phenols by adding HBr or Br_2; (3) by suitable bromination of o- and p-alkyl phenols, *e.g.*:

o-Oxy-mesityl chloride $C_6H_2[3, 5](CH_3)_2[2, 1](OH)CH_2Cl$, m.p. 58°. **o-Oxy-iso-duryl chloride** $C_6H[3, 5, 6](CH_3)_3[2, 1](OH)CH_2Cl$, m.p. 100°. **m-Bromo-o-oxy-benzyl bromide** $C_6H_3[3]Br[2,1](OH)CH_2Br$, m.p. 98°. **m,m-Dibromo-o-oxy-benzyl bromide** $C_6H_2[3, 5]Br_2[2, 1](OH)CH_2Br$, m.p. 117°. **Tribromo-o-oxy-benzyl bromide** $C_6HBr_3[2, 1](OH)CH_2Br$, m.p. 134°. **Tetrabromo-o-oxy-benzyl bromide** $C_6Br_4[2, 1](OH)CH_2Br$, m.p. 156°. **Dibromo-o-oxy-mesityl bromide** $C_6Br_2(CH_3)_2[2, 1](OH)CH_2Br$, m.p. 150°. **Bromo-o-oxy-iso-duryl bromide** $C_6Br(CH_3)_3[2, 1](OH)CH_2Br$, m.p. 112°. **m, m-Dibromo-p-oxy-benzyl bromide** $C_6H_2Br_2[4, 1](OH)CH_2Br$, m.p. 150°. **Dibromo-p-oxy-pseudo-cumyl bromide** $C_6Br_2(CH_3)_2[4, 1](OH)CH_2Br$, m.p. 126°. **Dibromo-p-oxy-mesityl bromide,** m.p. 147°. **Tetrachloro-p-oxy-benzyl bromide** $C_6Cl_4[4, 1](OH)CH_2Br$, m.p. 160°, and **chloride,** m.p. 146°. **Penta-, hexa,-** and **heptabromo-p-ethyl-phenol** $C_6HBr_3[4, 1](OH)CHBr*CH_2Br$, $C_6HBr_3[4, 1](OH)CHBr*CHBr_2$ and $C_6Br_4[4, 1](OH)CHBr*CHBr_2$, **Tetrabromo-iso-eugenol** $C_6HBr_2[3]OCH_3[4, 1](OH)CHBr*CHBrCH_3$. **Heptabromo-p-iso-propyl-phenol** $C_6Br_4[2, 1](OH)CBr*(CHBr_2)CH_3$, m.p. 183°, etc.

These substances are insoluble in alkalies, and show an abnormal mobility of one aliphatically linked Br atom. This Br atom, on treating with water, alcohol, glacial acetic acid, amines, potassium cyanide, or sulpho-hydrate, is easily exchanged for the residues OH, OAlK, $OCOCH_3$, NHR, CN, SH; with phenols, and tertiary amines of the dimethyl-aniline type, they transpose very easily, without condensing agents, into diphenyl-methane derivatives. A reactivity similar to that of the pseudo-phenol alcohols is possessed by the corresponding sulpho-cyanides, acetates, and nitro-bodies, such as $C_6Br_2(CH_3)_2[4, 1](OH)CH_2NO_2$ (B. **84,** 4264; cp. also the analogous behaviour of propenyl-phenyl dibromides). To explain the behaviour of these substances, called "*pseudo-phenols*" on account of their insolubility in alkalies, it is assumed that, in consequence of hitherto unexplained influences, the CH_2Br (or CHBr) group so closely approaches the para- or ortho-hydroxyl that, in most reactions, there is a splitting off of HBr in the first instance, leading to the formation of highly reactive "*methylene-quinones*" or "*quinone-methanes*" (B. **86,** 2336), which react further with addition of the agents; or the pseudo-phenol bromides are regarded as quinone-like substances, corresponding to the scheme:



Pseudo-phenol bromides **Methylene-quinones** **Phenol alcohols.**

In their other chemical properties the pseudo-phenols correspond exactly to the phenols, being easily converted into O-acetyl compounds and urethanes.

Methylene-quinones.—The methylene-quinones, assumed above as intermediate products, may be obtained from the o- and p-pseudo-phenol bromides by treatment with sodium acetate solution, or dilute alkaline hydroxide. The o-methylene-quinones are formed much more easily than the para-bodies, the latter easily passing into polymerised products, and, partly, into condensation products soluble in alkalies, *e.g.* derivatives of p_2-dioxy-diphenyl-methane.

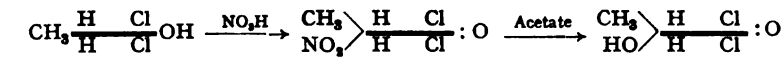
From the pseudo-bromides of p-ethyl-phenol, iso-eugenol, and p-iso-propyl-phenol, on the other hand, derivatives of *p-ethylidene-p-propylidene* and *p-iso-propylidene-quinone* can be isolated. The methylene-quinones are yellow substances, easily polymerised and bleached, by light or by acids. The chemical behaviour of the o- and p-methylene-quinones shows a remarkable difference. The para-bodies are highly reactive, easily combining with water, alcohols, acetic acid, and H haloids to form the corresponding phenol-alcohol derivatives; whereas the o-methylene-quinones are quite indifferent, so that they can hardly be regarded as intermediate products in the transformations of the o-pseudo-phenol haloids.

o-Iso-durylene-quinone CH_2 : [1]$C_6H(CH_3)_3$[2] : O, m.p. 129°. **Tetrabromo-o-methylene-quinone** CH_2 : [1]C_6Br [2] : O, m.p. *ca.* 130°. **Bromo-o-iso-durylene-quinone** CH_2 : [1]$C_6Br(CH_3)_3$[2] : O, m.p. 155°. **Dibromo-dimethyl-o-methylene-quinone** CH_2 : [1]$C_6Br_2(CH_3)_2$[2] : O, m.p. 168°. **Hexabromo-p-ethylidene-quinone** $CHBr_2CH$: [1]C_6Br [4] : O. **Tribromo-methoxy-p-propylidene-quinone** $CH_3CHBrCH$: [1]$C_6HBr_2(OCH_3)$[4] : O. **Heptabromo-p-iso-propylidene-quinone** $CH_3(CHBr_2)C$: [1]C_6Br_4[4] : O, m.p. 185°. Cp. also the much more stable methylene-quinones of the di- and triphenyl-methane series, *e.g.* diphenyl-methylene-quinone and quino-diphenyl-methane, the dyestuffs of the benzo-phenone and triphenyl-carbinol group, such as auramin, rosaniline, rosolic acid, etc., must be regarded as derivatives of methylene-quinone.

Literature.—See Auwers, A. **301,** 203; **334,** 264; **344,** 93; B. **32,** 2978; **34,** 4256; **36,** 1878; **38,** 3302; **39,** 3160; Zincke, A. **320,** 145; **322,** 174; **329,** 1; **349,** 67; **350,** 269; **353,** 357.

Quinols.—Related to the pseudo-phenols and methylene-quinones is the species of compounds known as *quinols*, which are also related to the quinones proper.

(1) Quinols were first obtained from para-alkylated bromine- or chlorine-substituted phenols, by oxidation with nitric acid or nitrogen oxides, the so-called nitro-ketones, or quinitrols, being intermediate products:

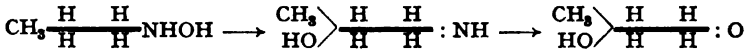


Dichloro-p-cresol — Dichloro-tolu-quinitrol — Dichloro-tolu-quinol.

Caro's acid also oxidises the non-substituted p-alkyl-phenols, like p-cresol, 2, 4-xylenol, in small quantities, to quinol (B. **36,** 2028).

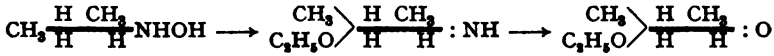
(2) The simplest representatives of this series were obtained from p-alkyl-phenyl-hydroxylamines by transposition with H_2SO_4; the

imine-quinols, obtained as intermediate products, become quinols, by splitting off NH_3:



p-Tolyl-hydroxylamine — Imino-tolu-quinol — Tolu-quinol.

Similarly, the p-alkyl-phenyl-hydroxylamines, heated with alcoholic H_2SO_4, give imino-quinol ether and quinol ether:



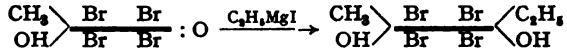
m-Xylyl-β-hydroxylamine — Imino-xylo-quinol-ethyl ether — Xylo-quinol-ethyl ether.

(3) Small amounts of quinols are also obtained from quinones, by the action of magnesium-methyl iodide.

The quinols are colourless substances, soluble in alkalies, and subject to acidulation; they are easily reduced to p-alkyl-phenols, from which they may be partly recovered by oxidation.

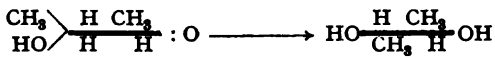
On the plan of the α, β-olefin-ketones, the simplest quinols combine with two molecules of hydroxylamine to form β-hydroxylamine-oximes (cp. Vol. I.). With phenyl-hydrazin, various substances are formed—according to the conditions, phenyl-hydrazino-compounds, diphenyl-hydrazones of diketo-oxy-tetrahydro-benzols, or azo-compounds with rejection of H_2O.

With alkyl-magnesium haloids the quinols yield *diquinols* by method 3 (above):



Tetrabromo-tolu-quinol — Tetrabromo-methyl-ethyl-diquinol.

The quinols have a characteristic tendency towards intramolecular atomic displacements. We may mention the migration of the para-alkyl group brought about by sulphuric acid, with formation of hydro-quinones:



2, 4-Dimethyl-quinol — p-Xylo-hydroquinone.

In the quinol ethers this transposition takes two directions, resorcin ethers being formed with migration of the alkoxyl group, besides hydro-quinone ethers, on heating with alcoholic H_2SO_4.

On heating with concentrated H_2SO_4, the halogen-substituted methyl-quinols split off formaldehyde, and pass into p_2-dioxy-diphenyl-methanes. An analogous behaviour is shown by the isomeric p-oxy-benzyl alcohols and their derivatives, the pseudo-phenol bromides, intermediate products being probably the methylene-quinones (A. **356**, 124). Tetrabromo-ethyl-quinol, on being treated with concentrated H_2SO_4, gives tribromo-ethyl-quinone (A. **341**, 262).

In the halogen-substituted quinols the halogen atom, occupying the o-position with reference to the quinol group, may be replaced by OH, NHC_6H_5, etc. (cp. chloranile).

Instead of the expected quinol, nitro-chloro-p-cresol yields *nitro-chloro-tolu-quinone* on heating with HNO_3, the quinol undergoing trans-

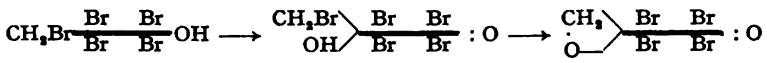
position to hydroquinone, and oxidation. Nitro-bromo- and nitro-dibromo-p-cresol behave similarly (A. **341,** 310). The atomic displacement may also take other directions, according to the structure of the quinols (cp. B. **35,** 443).

p-Tolu-quinol $CH_3(OH)[4]C_6H_4:O$, m.p. 75°, from p-tolyl-hydroxylamine with dilute sulphuric acid, and, in small quantities, from p-cresol with Caro's acid.

2, 4-Dimethyl-quinol $CH_3(OH)[4]C_6H_3[2](CH_3):O$, m.p. 73°, from m-xylyl-β-hydroxylamine, with cold dilute H_2SO_4, yields, on heating with acids or alkalies, or on illumination, p-xylo-hydroquinone. **2, 4-Dimethyl-quinol-ethyl ether** $CH_3(OC_2H_5)[4]C_6H_3[2](CH_3):O$, b.p.$_{12}$ 94°. **Imino-2, 4-dimethyl-quinol-ethyl ether** $CH_3(OC_2H_5)[4]C_6H_3[2](CH_3):NH$, b.p.$_{11}$ 98°, from m-xylyl-β-hydroxylamine with alcoholic H_2SO_4. **Mesityl-quinol** $CH_3(OH)[4]C_6H_2[2, 6](CH_3)_2:O$, m.p. 46°, from mesityl-hydroxylamine, is transposed into cumo-hydroquinone. **2, 4, 5-Trimethyl-quinol,** m.p. 116°, from pseudo-cumenol with Caro's acid, and from p-xylo-quinone with CH_3MgI (B. **36,** 2038). **Di-, tri-,** and **tetrachloro-tolu-quinols,** m.p. 123°, 90°, and 166°, from di-, tri-, and tetrachloro-p-cresol, with HNO_3, either direct, or by way of the quinitrols (method 1).

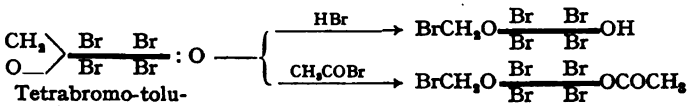
Di-, tri-, and tetrabromo-tolu-quinol, m.p. 134°, 128°, and 205°. On treating with alcoholic HCl, two bromine atoms are replaced by chlorine in the tetrabromo-tolu-quinol, and one Br atom in the tribromo-tolu-quinol, forming respectively : **dibromo-dichloro-tolu-quinol,** m.p. 162°, and **dibromo-chloro-tolu-quinol,** m.p. 135°. **Tetrabromo-ethyl-quinol** $C_2H_5(OH)[4]C_6Br_4:O$, m.p. 140°. **Tetrabromo-methyl-ethyl-diquinol** $CH_3(OH)[1]C_6Br_4[4](OH)C_2H_5$, m.p. 191°, and **tetrabromo-diethyl-quinol** $C_2H_5(OH)[1]C_6Br_4[4](OH)C_2H_5$, m.p. 180°, are formed from tetrabromo-ethyl-quinol with methyl- and ethyl-magnesium iodide respectively.

The pseudo-phenol bromides also are oxidised by HNO_3 to quinols, which, on treatment with alkalies or silver oxide, yield oxides with rejection of HBr.



Pentabromo-p-cresol — Pentabromo-tolu-quinol — Pentabromo-tolu-quinol oxide.

These oxides add HBr and acetyl bromide, with formation of hydroquinone derivatives :



Tetrabromo-tolu-quinol oxide.

Literature.—Cp. Auwers, B. **35,** 425, 443; Bamberger, B. **33,** 3600; **35,** 1424, 3886; **36,** 1625; **40,** 1890, 2236; Zincke, B. **34,** 253; A. **328,** 261; **343,** 100; **341,** 309.

Dioxy-benzyl alcohols are not known in a free condition, but derivatives of 2, 5-dioxy- and of 3, 4-dioxy-benzyl alcohol have been obtained in the reduction of certain aldehyde ethers with sodium amalgam. **Di-methyl-gentisin alcohol** $(CH_3O)_2[2, 5]C_6H_3[1]CH_2.OH$ boils at 278°.

Vanillyl alcohol $CH_3O[3]HO[4]C_6H_3[1]CH_2.OH$, from vanillin, melts at 115°.

Piperonyl alcohol $CH_2\langle{O[3] \atop O[4]}\rangle C_6H_3[1]CH_2.OH$, from piperonal, melts at 51°. **Homo-piperonyl alcohol** $CH_2\langle{O[3] \atop O[4]}\rangle C_6H_3CH_2CH_2OH$, b.p.$_{10}$ 156°, see B. **41**, 2752. **o-Dioxy-benzyl-amine** melts at 168° (B. **27**, 1799).

(2) AROMATIC OXY-MONO-ALDEHYDES, PHENOL-ALDEHYDES.

The phenol-aldehydes are obtained (1) by oxidising the phenol alcohols with chromic acid; (2) by an important nuclear-synthetic method, consisting in letting chloroform and an alkaline hydroxide act upon phenols (reaction of Reimer), when the chloroform enters the o- and p-position with reference to the phenol-hydroxyl, and is then converted into the aldehyde group (B. **9**, 1268):

$$C_6H_5.OH+CHCl_3+4KOH = C_6H_4\langle{OK \atop CHO}+3KCl+3H_2O.$$

On treating o- and p-alkylated phenols with chloroform and alkali, some chlorinated products of a ketone type, insoluble in alkalies, are produced besides the phenol-aldehydes, *e.g.*

$$CH_3\text{-}\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{-}OH \longrightarrow \underset{CHCl_2}{\overset{CH_3}{>}}\underset{H}{\overset{H}{C}}\text{-}\underset{H}{\overset{H}{C}}\text{:O}.$$

These substances should be regarded as derivatives of keto-dihydrobenzol, and are dealt with in that connection.

(3) A nuclear synthesis of phenol-aldehydes is also brought about by the action of prussic acid and gaseous HCl upon the phenols, or their ethers, with or without Al chloride; aldimines are first formed, and these are easily converted into aldehydes (Gattermann, A. **357**, 313):

$$C_6H_5OH \xrightarrow{HNC(HCl)} HN:CH.C_6H_4OH \longrightarrow OCH.C_6H_4OH.$$

By similar reactions, oximes of phenol-aldehydes are produced (3*a*) from multivalent phenols, mercury fulminate, and HCl; and phenyl-imines of aldehydes (3*b*) from multivalent phenols, formanilide, and $POCl_3$:

$$C_6H_4(OH)_2 \begin{cases} \xrightarrow{HON:C(HCl)} C_6H_3(OH)_2CH:NOH \\ \xrightarrow{C_6H_5N:CHCl} C_6H_3(OH)_2CH:NC_6H_5 \end{cases}.$$

Behaviour.—All the phenol-aldehydes show the same reactions of the aldehyde group as the benzaldehydes. Oxidising agents convert them with difficulty into phenol-carboxylic acids; this is most easily accomplished by fusion with caustic alkalies. They reduce an ammoniacal silver solution, but not the Fehling solution. On oxidation with dilute alkaline H_2O_2 solution the o- and p-phenol-aldehydes split off the aldehyde group and easily pass into pyro-catechin and hydroquinone (C. 1910, I. 634). They dissolve in alkalies, forming salts—*e.g.* $C_6H_4(CHO).ONa$; the alkyl iodides convert the latter into alkyl ethers.

(*a*) **Monoxy-benzaldehydes** $HO.C_6H_4.CHO$.—Three are possible according to theory; all of them are known. Anisic aldehyde, the

methyl ether of p-oxy-benzaldehyde, has been known for the longest period.

Salicylic aldehyde, *o-oxy-benzaldehyde,* formerly called *salicylous* or *spiroylous* acid, boils at 196°. Its sp. gravity equals 1·172 (15°). It occurs in the volatile oils of the different varieties of *Spiræa—e.g. Spiræa ulmaria.* It is obtained by the oxidation of saligenin and salicin (Piria, 1839) and by the decomposition of *helicin,* an oxidation product of salicin (*q.v.*). Also by reduction of sodium salicylate with sodium amalgam in the presence of free boric acid (B. **41,** 4147, 4148). It is most readily prepared (together with p-oxy-benzaldehyde) by the action of chloroform and caustic potash upon phenol. It is separated from the p-body by distillation in steam, in which salicylic aldehyde is very volatile. It is rather easily soluble in water; the solution is coloured a deep violet by ferric chloride (compare saligenin and salicylic acid). In alkalies it dissolves with an intense yellow coloration, in contrast with p-oxy-benzaldehyde (B. **39,** 3087)). Like all ortho-oxy-aldehydes, it colours the skin an intense yellow. Sodium amalgam transforms it into saligenin; oxidising agents change it to salicylic acid.

Potassium-salicylic aldehyde $C_6H_4(OK)CHO+H_2O$ consists of yellow plates. The *methyl ether* $C_6H_4(O.CH_3).CHO$ melts at 35° and boils at 238°; the *ethyl ether* boils at 248°. The *aceto-derivative* $CH_3.CO.O.C_6H_4.CHO$ melts at 37° and boils at 253°. *Glucose derivative,* see *Helicin. o-Aldehydo-phenoxy-acetic acid* $CO_2H.CH_2O[2]C_6H_4[1]CHO$, melting at 132°, splits off water and becomes cumarilic acid (*q.v.*). *Salicyl-aldoxime* melts at 57°; cp. **B. 22,** 3320. *o-Anisaldoxime* $CH_3O.[2]C_6H_4[1]CH:N(OH)$, m.p. 92° (B. **23,** 2741); also obtained from anisol, mercury fulminate, and hydrated $AlCl_3$ besides p-anisaldoxime (B. **23,** 2741; **36,** 648). **Salicyl-hydramide** $(C_7H_6O)_3N_2$, m.p. 167° (C. 1899, II. 827; 1900, I. 123). **Salicyl-hydrazone** $HO.C_6H_4CH:NNH_2$, m.p. 96°. **o-Oxy-benzalazin** $HOC_6H_4CH:N.N:CHC_6H_4OH$, m.p. 213° (B. **31,** 2806). **Phenyl-hydrazone,** m.p. 142°, b.p.$_{28}$ 234°, decomposes on distillation partly into aniline and salicylic acid nitrile $C_6H_4(OH)CN$ (B. **36,** 580). Nitro-salicyl-aldehyde, see B. **22,** 2339.

m-Oxy-benzaldehyde, m.p. 104°, b.p. 240°, results from the reduction of m-oxy-benzoic acid with sodium amalgam (B. **14,** 969) and from m-nitro-benzaldehyde (B. **15,** 2045). Its *oxime* melts at 87°. Its *phenyl-hydrazone* melts at 130° (B. **24,** 826). See B. **18,** 2572, for the nitro-m-methoxy-benzaldehydes.

p-Oxy-benzaldehyde is formed from phenol, chloroform, and caustic alkali, together with salicylic aldehyde. It melts at 116°, and sublimes. Its *aldoxime* melts at 65°; its *hydrazone* at 178°. Consult B. **29,** 2302, 2355, for the haloid p-oxy-benzaldehydes. Its methyl ether, readily accessible, is the so-called:

Anisic aldehyde, *p-methoxy-benzaldehyde* $CH_3O[4]C_6H_4[1]CHO$, b.p. 248°, with sp. gr. 1·128 (15°). It results in oxidising anethol (*q.v.*), present in various essential oils (anise, fennel, tarragon, etc.), with dilute nitric acid or a chromic acid mixture (C. 1900, I. 255).

p-Anisaldoxime, m.p. 61°, from anisol, mercury fulminate, and hydrated $AlCl_3$, besides o-anisaldoxime and p-anisic nitrile. **p-Ethoxy-benzaldoxime** $(C_2H_5O)[4]C_6H_4CH:NOH$, obtained in two forms, melting at 118° and 157° respectively, from phenetol, mercury fulminate,

and $AlCl_3$ (B. **36**, 648, 650). **Anisal chloride** $CH_3O.C_6H_4.CHCl_2$, m.p. 20° (B. **41**, 2331).

Homologous monoxy-benzaldehydes have been prepared from various phenols by Reimer's method, and also by Gattermann's method :

		M.p.	B.p.
o-Homo-salicyl-aldehyde	$CH_3[3]C_6H_3[2]OH[1]CHO$	17°	208° [1]
α-m-Homo-salicyl-aldehyde	$CH_3[4]C_6H_3[2]OH[1]CHO$	59°	220° [2]
β-m-Homo-salicyl-aldehyde	$CH_3[6]C_6H_3[2]OH[1]CHO$	31°	229° [2]
p-Homo-salicyl-aldehyde	$CH_3[5]C_6H_3[2]OH[1]CHO$	56°	217°
o-Homo-p-oxy-benzaldehyde	$CH_3[5]C_6H_3[4]OH[1]CHO$	115° [3]	
p-Homo-p-oxy-benzaldehyde	$CH_3[2]C_6H_3[4]OH[1]CHO$	110°	
Trimethyl-salicyl-aldehyde	$(CH_3)_3[3, 5, 6]C_6H[2]OH[1]CHO$	105° [4]	
p-Thymotin-aldehyde	$CH[2]C_3H_7[5]C_6H_2[4]OH[1]CHO$	133° [5]	
p-Carvacrotin-aldehyde	$CH[5]C_3H_7[2]C_6H_2[4]OH[1]CHO$	liquid [6]	
p-Iso-butyl-salicyl-aldehyde	$C_4H_{11}[4]C_6H_3[2]OH[1]CHO$	„	252°.[7]

Literature.—[1] B. **24**, 3667 ; [2] C. 1906, I. 1012 ; [3] B. **24**, 3667 ; [4] B. **18**, 2656 ; **32**, 3598 ; [5] B. **16**, 2097 ; **31**, 1767 ; [6] B. **19**, 14 ; [7] B. **28**, R. 468.

p-Oxy-mesitylene-aldehyde $(CH_3)_2[3, 5](OH)[4]C_6H_2CHO$, m.p. 114°, from mesitol by oxidation with **ethyl nitrite** ; oxime, m.p. 169° (A. **311**, 363).

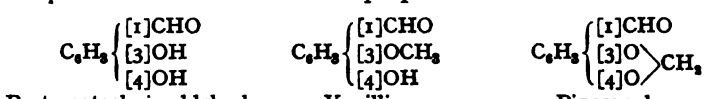
The o-oxy-benzaldehydes are more readily soluble in water and more sparingly soluble in chloroform than the p-oxy-benzaldehydes. The o-bodies are volatile in steam, form sparingly soluble sodium bisulphite derivatives, and are coloured yellow by ammonia (B. **11**, 770).

The phenyl-hydrazones of homo-salicyl-aldehydes and other salicyl-aldehydes with alkylated nucleus are, strangely enough, insoluble in alkalies (B. **35**, 4099).

p-Methoxy-phenyl-acetaldehyde $CH_3O[4]C_6H_4CH_2CHO$. The oxime of this aldehyde is obtained by the reduction of anisylidene-nitro-methane $CH_3OC_6H_4CH : CHNO_2$ (C. 1902, II. 449).

p-Methoxy-hydratropa-aldehyde $CH_3O[4]C_6H_4CH(CH_3)CHO$, b.p. 256°, from anethol $CH_3OC_6H_4CH : CHCH_3$ by oxidation with HgO and iodine, with migration of the aromatic residue (C. 1902, I. 1056).

(*b*) **Dioxy-benzaldehydes.**—Some of the dioxy-benzaldehydes which have been prepared by the chloroform-potash reaction are ethereal derivatives of proto-catechuic aldehyde, and are characterised by an agreeable odour. This is especially true of *vanillin* and *piperonal*, or *heliotropine*. Both substances are prepared on a technical scale :



Proto-catechuic aldehyde — Vanillin — Piperonal.

Proto-catechuic aldehyde, [3, 4]-*dioxy-benzaldehyde*, m.p. 153° (B. **26**, R. 701), was first obtained from piperonal (Fittig and Remsen, 1871) ; also from vanillin, iso-vanillin, and opianic acid by heating with hydrochloric acid, and by the action of H_2O_2 upon m- and p-oxy-benz-aldehyde (C. 1904, II. 1631). It is prepared in the nuclear-synthetic way from pyro-catechin by the chloroform reaction. It dissolves readily in water. Ferric chloride colours its aqueous solution a deep green. It reduces ammoniacal silver solutions. Molten caustic potash

converts proto-catechuic aldehyde into proto-catechuic acid. Its *phenyl-hydrazone* exists in two modifications: α- (stable), melting at 176°, and β- (unstable), melting at 121°–128°. Its *oxime* melts at 150° (B. **29**, R. 670). Proto-catechuic-aldehyde-carboxylate $(CO)O_2 : C_6H_3CHO$, m.p. 124°, b.p.$_{13}$ 162°.

Vanillin, *m-methoxy-p-oxy-benzaldehyde,* m.p. 80°, sublimes readily, and is the active constituent of the vanilla bean pod (*Vanilla planifolia*), which contains about 2 per cent. of it (B. **9**, 1287). **Vanillin** also occurs in the orchid *Nigritella suaveolens* (B. **27**, 3049). It was first prepared artificially from the glucoside coniferine by its oxidation with chromic acid (Tiemann and Haarmann, 1874; B. **7**, 613). Glyco-vanillin was obtained as an intermediate product in the oxidation of coniferine; acids or emulsin split it up into glucoses and vanillin (B. **18**, 1595, 1657). Vanillin is also produced by oxidising eugenol (*q.v.*) (B. **9**, 273). In the nuclear-synthetic way it has also been formed, together with m-methoxyl-salicylic aldehyde, boiling at 266°, from guaiacol, chloroform, and caustic potash (B. **14**, 2023; C. 1910, I. 1881). Industrially, it is obtained on a large scale by the oxidation of iso-eugenol, obtained by the transposition of eugenol, contained in abundance in carnation oil. It is advantageous to protect the free hydroxyl from oxidation by the temporary introduction of an acid residue (CH_3CO, $C_6H_5SO_2$, etc.):

C_6H_3 {[1]$CH_2.CH : CH_2$, [3]OCH_3, [4]OH} ⟶ C_6H_3 {[1]$CH : CH.CH_3$, [3]OCH_3, [4]OH} ⟶ C_6H_3 {[1]CHO, [3]OCH_3, [4]OH}

Eugenol — Iso-eugenol — Vanillin.

Heated with HCl, vanillin splits up into proto-catechu-aldehyde and CH_3C. It behaves as a p-oxy-benzaldehyde and, when fused with KHO, it passes into proto-catechuic acid—two facts which determine its constitution. By sodium amalgam, vanillin is converted into vanillyl alcohol, and into hydra-vanilloïn, which corresponds to hydro-benzoïn.

Vanillin-oxime melts at 117° (B. **24**, 3654).

Trithio-vanillin $[C_6H_3(OH)(OCH_3)CSH]_3$ melts at 236° (B. **29**, 143).

Iso-vanillin, *p-methoxy-m-oxy-benzaldehyde,* melting at 116°, smells, when heated, like vanilla and anise oil. It is obtained by oxidising hesperitinic acid, or by heating opianic acid with hydrochloric acid.

Methyl-vanillin $(CH_3O)_2C_6H_3CHO$, m.p. 42°, b.p. 283° (B. **11**, 662).

Piperonal, *proto-catechuic aldehyde-methylene ether, heliotropine* $(CH_2O_2)C_6H_3CHO$, melting at 37° and boiling at 263°, was obtained by the oxidation of piperic acid (*q.v.*). It is also formed by treating proto-catechuic aldehyde with alkali and methylene iodide. Industrially, it is obtained from safrol (*q.v.*) as vanillin is obtained from eugenol. Its odour is pleasant, like that of heliotrope. Piperonylic acid results from its oxidation, and piperonyl alcohol from its reduction. On heating with dilute mineral acids to 190°, under pressure, it breaks up into proto-catechuic aldehyde and formaldehyde or methyl alcohol (C. 1905, II. 1060). Its *oxime* melts at 110°. Its *phenyl-hydrazone* melts at 100°. PCl_5 converts it into **piperonal chloride** $(CH_2O_2)C_6H_3CHCl_2$, and **di-chloro-piperonal chloride** $(CCl_2O_2).C_6H_3CHCl_2$, which is changed by cold water into the **carboxylate** of **proto-catechuic aldehyde chloride** $(CO)O_2$:

$C_6H_3CHCl_2$, m.p. 97°, b.p.$_{15}$ 178°, also obtained direct from piperonal with thionyl chloride at 220°, or by heating with chloride of sulphur (B. **42,** 417). **Bromo-piperonal** $(CH_2O_2).C_6H_2Br.CHO$ (B. **24,** 2592). **o-Nitro-piperonal** yields bidioxy-methylene indigo (B. **24,** 617).

Homo-piperonal $(CH_2)O_2 : C_6H_3CH_2CHO$, m.p. 69°, b.p.$_{10}$ 144°, is formed by the oxidation of safrol (*q.v.*) with ozone (B. **41,** 2751). Its oxime, m.p. 120°, is formed from piperonylidene-nitro-methane by reduction with Al amalgam (C. 1902, II. 449).

Concerning nitro-proto-catechuic aldehyde, nitro-vanillin, amino-vanillin, and derivatives, see C. 1902, II. 31; B. **36,** 2930.

The following bodies have been prepared from resorcin and hydroquinone by the action of chloroform and caustic alkali, just as proto-catechuic aldehyde was made from pyro-catechin :

β-Resorcyl-aldehyde $(HO)_2[2, 4]C_6H_3[1]CHO$ melts at 135°.
Orcyl-aldehyde $(HO)_2[2, 4]C_6H_2[5, 1](CH_3)CHO$, m.p. 180°, from hydroquinone with chloroform and alkali.
Gentisin-aldehyde $(HO)_2[2, 5]C_6H_3[1]CHO$ melts at 99°.

Dioxy-aldehydes are also produced in dilute solutions when much chloroform and caustic potash are used. The monomethyl ethers of resorcin and hydroquinone, like guaiacol, each yield, upon treatment with chloroform and potash, two aldehydes: one, comparable in deportment with salicyl-aldehyde, contains the aldehyde group in the o-position with reference to phenol-hydroxyl; while the other contains the aldehyde group in the p-position, referred to the free phenol-hydroxyl (B. **14,** 2024).

Gentisin-aldehyde is also produced by oxidation of salicyl-aldehyde with potassium persulphate in alkaline solution (C. 1907, II. 901). The anile of resorcyl-aldehyde $C_6H_3[2, 4](OH)_2CH : NC_6H_5$, m.p. 126°, is also obtained from resorcin with formanilide and $POCl_3$, and the oxime $C_6H_3(OH)_2CH : NOH$ with mercury fulminate and HCl.

(*c*) **Tri- and Tetra-oxy-benzaldehydes.**—From pyrogallol, phloroglucin, and oxy-hydroquinone the corresponding aldehydes have been obtained with HCN and HCl : **Pyrogallol-aldehyde,** *gallic aldehyde* $(HO)_3[2, 3, 4]C_6H_2CHO$, m.p. 161°. **Phloro-glucin-aldehyde** $(HO)_3[2, 4, 6]C_6H_2.CHO$, decomposed on melting. **Oxy-hydroquinone-aldehyde** $(HO)_3[2, 4, 5]C_6H_2.CHO$, m.p. 223° (B. **32,** 278). The oximes and aniles of these aldehydes have also been obtained synthetically by methods 3*a* and 3*b*. Alkyl ethers of these bodies have been formed by oxidising aromatic plant derivatives, containing unsaturated aliphatic side chains (B. **16,** 2112; **17,** 1086; **24,** 3818; **41,** 1918).

Glyco-syringa-aldehyde, an oxidation product of *syringine* (*q.v.*), when treated with emulsin yields **4-oxy-3, 5-dimethoxy-benzaldehyde,** *syringa-aldehyde* (B. **22,** R. 107).

2, 4, 5-Trimethoxy-benzaldehyde, *asaryl-aldehyde,* m.p. 114°, is obtained by oxidising *asarone* (propenyl-trimethoxy-benzol), and from oxy-hydroquinone-trimethyl ether, with HCN, HCl, and $AlCl_3$ (B. **32,** 289; **39,** 1211).

(3) Phenol Ketones.

They have been obtained (1) from amido-ketones (B. **18,** 2691); (2) from aromatic β-ketone-carboxylic acids (B. **25,** 1308); (3) by the

breaking up of C-alkylated benzo-tetronic acids with concentrated alkalies (A. **379,** 333) ; (4) from the dibromides of the propenyl-phenols and their ethers : (*a*) by transforming into bromo-hydrins and ethylene oxides, and transposing the latter with acids or by heating alone (B. **38,** 3464) :

$$\underset{\dot{C}_6H_4OCH_3}{CHBr.CHBrCH_3} \xrightarrow{H_2O} \underset{\dot{C}_6H_4OCH_3}{CH(OH).CHBrCH_3} \xrightarrow{KOH} \underset{\dot{C}_6H_4OCH_3}{\overline{\dot{C}H.O.\dot{C}H}.CH_3} \longrightarrow \underset{\dot{C}_6H_4OCH_3}{CH_2.CO.CH_3}$$

(*b*) by transforming into ethyl bromo-hydrins and α-ethoxy-propenyl-phenols by sodium ethylate, and saponifying the latter :

$$\underset{C_6H_4OCH_3}{CHBr.CHBrCH_3} \xrightarrow{C_2H_5ONa} \underset{\dot{C}_6H_4OCH_3}{CH(OC_2H_5).CHBr.CH_3} \xrightarrow{C_2H_5ONa}$$

$$\underset{\dot{C}_6H_4OCH_3}{C(OC_2H_5) : CHCH_3} \longrightarrow \underset{\dot{C}_6H_4OCH_3}{CO.CH_2.CH_3}$$

To these must be added the methods of nuclear synthesis consisting in the introduction of acid radicles into phenols, and phenol-alkyl ethers ; (5) condensation of phenols with glacial acetic acid, and other aliphatic acids, with the aid of zinc chloride or tin tetrachloride (B. **14,** 1566 ; **23,** R. 43 ; **24,** R. 770), or, better, by phosphorus oxy-chloride (B. **27,** 1983) ; (6) from phenols with acid chlorides and, preferably, the addition of zinc chloride (B. **22,** R. 746 ; C. 1904, I. 1597) ; (7) from phenol-alkyl ethers or phenols and acid chlorides in the presence of $AlCl_3$ (B. **36,** 3890 ; C. 1898, I. 1223) ; excess of $AlCl_3$ saponifies the resulting phenol ethers to oxy-ketones. Starting from the thio-phenol ethers, thio-phenol mono-ketones are obtained by this method (C. 1908, II. 1659)

o-Oxy-aceto-phenone, b.p. 213°, is formed by method 2. **p-Oxy-aceto-phenone,** m.p. 107°, is produced by method 1. **p-Acetyl-anisol,** *p-methoxy-aceto-phenone,* m.p. 38° and b.p. 258°, is formed by method 3. **Propionyl-phenol** $HOC_6H_4COC_2H_5$, m.p. 148°, is produced by method 4.

Aceto-pyro-catechol $(HO)_2[3, 4]C_6H_3[1]CO.CH_3$, melts at 116° (B. **27,** 1989). **Aceto-vanillon** $HO[4](CH_3O)[3]C_6H_3[1]COCH_3$, m.p. 115°, is produced in the oxidation of aceto-eugenol, and, synthetically, from guaiacol by method 7, or by condensation of benzoyl-vanillin with CH_3MgI, oxidation, and rejection of the benzoyl group (B. **24,** 2855, 2869). **Aceto-veratron** $(CH_3O)_2C_6H_3.CO.CH_3$, m.p. 48° (B. **27,** 1989). **Aceto-piperone** $(CH_2O_2)[3, 4]C_6H_3[1]CO.CH_3$, m.p. 87°, results on oxidising proto-cotoïn with potassium permanganate (B. **24,** 2989 ; **25,** 1127 ; **26,** 2348).

Resaceto-phenone $(HO)_2[2, 4]C_6H_3[1]CO.CH_3$, m.p. 142°, is produced by method 5, and from β-methyl-umbelliferone upon fusion with caustic potash (B. **16,** 2123). Its p-methyl ether, **pæonol** $CH_3O[4](HO)[2]C_6H_3.CO.CH_3$, m.p. 45°, occurs in the root-bark of *Pæonia Moutan,* a ranunculus from Japan (B. **25,** 1292). When resorcin-diethyl ether is acetylated with the aid of aluminium chloride the products are **1, 2, 4-resaceto-phenone-diethyl ether,** m.p. 69°, and an *isomeric* resaceto-phenone with the melting-point 178° (B. **29,** R. 386). Consult B. **29,** R. 674, for haloid resaceto-phenones.

Ore-aceto - phenone - dimethyl ether $CH_3[1]C_6H_2[3, 5](OCH_3)_2[4]$

$COCH_3$, m.p. 89°, and **isoro-aceto-phenone-dimethyl ether** $CH_3[1]C_6H_2[3, 5](OCH_3)_2[2]COCH_3$, m.p. 48°, from orcin-dimethyl ether by method 7 (B. **41**, 793).

Quina-aceto-phenone $(HO)_2[2, 5]C_6H_3[1]CO.CH_3$, m.p. 202°, is produced by method 2. **Valero-hydroquinone** $(HO)_2[2, 5]C_6H_3.CO.C_4H_9$, m.p. 115°. Its quin-hydrone results when sunlight acts upon benzo-quinone and valeric aldehyde (B. **24**, 1344).

Gall-aceto-phenone $(HO)_3[2, 3, 4]C_6H_2[1]CO.CH_3$, m.p. 168°, is formed by method 3 (B. **27**, 2737; **43**, 1016).

Anis-acetone, *p-methoxy-phenyl-acetone* $CH_3O[4]C_6H_4CH_2COCH_3$, b.p. 261°–265°, is found in aniseed oil (?) (C. 1902, II. 1256).

o-Acetyl-thio-phenol $HS[2]C_6H_4[1]COCH_3$, b.p. about 124°, from o-amido-aceto-phenone by way of the diazo-compound; yields thio-indigo during oxidation in alkaline solution, as well as the dithio-compound.

(4) Phenol-monocarboxylic Acids.

The aromatic oxy-acids, containing hydroxyl united to the benzene nucleus, combine the character of acids and phenols, hence are designated *phenol acids*. Should the hydroxyl groups enter the aliphatic side chains, we would obtain aromatic alcohol acids, showing in their behaviour very great similarity to the oxy-fatty acids.

Formation.—A. *From substituted carboxylic acids, as in the case of the phenols:* (1) Through the conversion of the amido-acids, by means of nitrous acid, into diazo-compounds, and then boiling the latter with water. (2) By fusing the sulpho-benzoic acids and halogen-benzoic acids with alkalies. (3) By oxidation of the benzoic acids, in the form of Am salts, with H_2O_2, o-, m-, and p-oxy-benzoic acids being formed together (C. 1907, II. 2046).

B. *From compounds in which the phenol-hydroxyl is already present:* (4) By fusing homologous phenols with alkalies, when the methyl group, linked to the nucleus, will be oxidised to the carboxyl group. (5) By oxidising the sulphuric or phosphoric acid esters of homologous phenols, and then saponifying the resulting phenol-carboxylic esters. (6) By fusing the phenol-aldehydes, difficult to oxidise, with alkalies. (7) By converting the phenol-aldoximes into oxy-acid nitriles, and then saponifying the latter.

C. *Nuclear Synthesis.*—(8) By the action of carbon dioxide upon the dry sodium salts of the phenols, at elevated temperatures, when the carbonic acid generally enters the ortho-position with reference to the hydroxyl group. This reaction will be more exhaustively discussed in connection with salicylic acid.

(9) By boiling the phenols with carbon tetrachloride and caustic potash (B. **10**, 2185):

$$C_6H_5.OH+CCl_4+5KOH = C_6H_4\langle^{OH}_{CO_2K}+4KCl+3H_2O.$$

The carboxyl usually occupies the p-position to the phenol-hydroxyl.

This reaction is perfectly analogous to that of the formation of oxaldehydes by means of chloroform and caustic alkali. The action of carbon tetrachloride upon p-alkylated phenols in the presence of $AlCl_3$ yields derivatives in both cases of keto-dihydro-benzol

$CH_2 \diagdown H\ H$ / $CCl_2 \diagup H\ H$: O, from which the phenols are regenerated on reduction (B. **41**, 897).

(10) When urea chloride, phenyl iso-cyanate, and phenyl-mustard oil, together with aluminium chloride, act upon phenol ethers (or thio-phenol ethers) in carbon disulphide solution (A. **244**, 61; B. **27**, 1733), the products are amides, anilides, and thio-anilides of alkyl-oxy-acids.

Behaviour.—They are monobasic acids. The hydrogen of the carboxyl group is alone replaced by metals when they are acted upon with alkaline carbonates.

Their hydroxyl hydrogen can also be replaced by alkalies, forming *basic* salts—*e.g.* $C_6H_4\langle^{ONa}_{CO_2Na}$. Carbon dioxide, however, will convert the latter into *neutral* salts. The ether esters manifest a like deportment, inasmuch as it is only the alkyl ester which is eliminated, with the production of a salt of an alkyl-ether acid :

$$C_6H_4\langle^{O.CH_3}_{CO_2.CH_3} + KOH = C_6H_4\langle^{O.CH_3}_{CO_2K} + CH_3.OH.$$

The o-oxy-acids, unlike the m- and p-derivatives, volatilise in aqueous vapour, are coloured violet by ferric chloride, and dissolve in chloroform. The m-oxy-acids are coloured reddish brown when heated with concentrated sulphuric acid, with the formation of oxy-anthraquinones (B. **18**, 2142). They are usually more stable than the o- and p-acids. Boiling concentrated hydrochloric acid decomposes the p-acids into carbon dioxide and phenols. All the oxy-acids decompose into carbon dioxide and phenols when distilled with lime.

A. **Monoxy-monocarboxylic Acids.**—Salicylic acid or o-oxy-benzoic acid is by far the most important representative of this class. It is extensively applied both in therapeutics and in the colour industry.

Monoxy-benzoic Acids.—The three isomerides theoretically possible are known.

Salicylic acid, o-oxy-benzoic acid $HO[2]C_6H_4[1]CO_2H$, melting at 155°, occurs in a free condition in the buds of *Spiræa ulmaria*, as the methyl ester in oil of *Gaultheria procumbens* (oil of evergreen), a species of Ericaceæ. It is produced, by the general methods of formation, (1) from anthranilic acid; (2) from o-sulpho-, o-chloro-, and o-bromo-benzoic acids; (3) from o-cresol; (4) from saligenin and salicyl-aldehyde; (5) from phenolates with CO_2; and (6) with carbon tetrachloride.

It is also formed upon fusing *cumarin* (*q.v.*) and *indigo* (*q.v.*) with caustic potash, and in the distillation of copper benzoate.

Technical Preparation.—Two methods of bringing sodium phenolate and CO_2 in reaction are applicable for this purpose :

(*a*) Sodium phenoxide is heated in a current of carbon dioxide at 180°–220°, when the latter is absorbed. Half of the phenol distils over, and the residue consists of disodium salicylate (H. Kolbe) :

$$2C_6H_5ONa + CO_2 = C_6H_4\,{}^{CO_2Na}_{ONa} + C_6H_5OH.$$

The behaviour of potassium phenolate in this reaction is remarkable. At 150° dipotassium salicylate is produced. At a more elevated temperature, however, there is formed with the dipotassium salicylate

its isomeride, dipotassium para-oxy-benzoate. The latter is more abundant in proportion to the increased temperature, until at 220° it is the sole product. The primary alkali salicylates, when heated, show the following behaviour.

Monosodium salicylate at 220° yields disodium salicylate, phenol, and CO_2 :

$$2C_6H_4\begin{matrix}CO_2Na\\OH\end{matrix} = C_6H_4\begin{matrix}CO_2Na\\ONa\end{matrix} + C_6H_5OH + CO_2.$$

Primary potassium salicylate at 220° yields phenol, dipotassium para-oxy-benzoate, and CO_2.

Primary sodium para-oxy-benzoate at 280° yields phenol, CO_2, and disodium salicylate (*J. pr. Ch.* 2, **16**, 425).

(*b*) Sodium phenoxide is saturated under pressure, in closed vessels, with carbon dioxide, when it is converted into sodium pheno-carbonate $C_6H_5.O.CO_2Na$. This is transformed, under pressure, at a temperature of 120°–130°, into phenol-sodium-o-carboxylic acid NaO[2]C_6H_4[1]COOH (R. Schmitt, German patent 29,939). This can be combined in one process by letting CO_2 act, under pressure, upon sodium phenate at 120°–140° (German patent 38,742). The second method gives a complete transformation of the phenol employed. This difference is probably due to the fact that, in Kolbe's method, the phenol-sodium-o-carboxylic acid first formed at the high temperature forms disodium salicylate and free phenol with the sodium phenate (B. **38**, 1375; **39**, 14; A. **351**, 313).

History.—Piria first obtained salicylic acid in 1838, when he oxidised its aldehyde with molten caustic potash (A. **30**, 165). In 1843 Cahours proved that evergreen oil consisted almost entirely of methyl-salicylic ester (A. **53**, 332). Gerland, in 1853, showed that anthranilic acid, as suspected by A. W. Hofmann, could be converted by nitrous acid into salicylic acid (A. **86**, 147). In 1860 H. Kolbe and Lautemann prepared it synthetically from phenol, sodium, and carbonic acid (A. **115**, 201). It was Kolbe who first correctly interpreted salicylic acid to be a monobasic oxy-acid, and, in 1874, discovered that the acid could readily be formed upon conducting carbon dioxide over dry heated sodium phenate. It was in this way that he ascertained the conditions necessary for the production of the acid upon a commercial scale.

Properties and Behaviour.—Salicylic acid crystallises from alcohol in colourless prisms; from hot water in long needles. It has a sweet acid taste. It dissolves in 400 parts of water at 15°, and in 12 parts at 100°; it is very soluble in chloroform. When it is heated alone, *salol*, or phenyl-salicylic ester, and *xanthone* (*q.v.*) are produced (A. **269**, 323). Sodium in amyl-alcohol solution reduces it to normal pimelic acid. In this reaction the ring is ruptured, and cyclo-hexanone-carboxylic acid appears as an intermediate product (B. **27**, 331).

Its aqueous solution acquires a violet coloration upon the addition of ferric chloride (C. 1908, II. 1511). It is a powerful antiseptic, arrests decay and fermentation (Kolbe, *J. pr. Ch.* 2, **10**, 9), and is applied therapeutically both as the free acid and in the form of its sodium salt (in rheumatoid arthritis).

Salicylates.—**Sodium salicylate** $HO.C_6H_4CO_2Na$ is a crystalline powder, with an unpleasant sweet taste. **Basic calcium salicylate**

$(OC_6H_4CO_2)Ca+H_2O$ dissolves with great difficulty, and is precipitated upon boiling salicylic acid with lime water. It serves for the separation of salicylic acid from m- and p-oxy-benzoic acids.

Esters, Ethers, and Ether Esters.—**Methyl ester** $HO.C_6H_4.CO_2CH_3$, boiling at 224°, with sp. gr. 1·197 (0°), is the chief ingredient of evergreen oil (from *Gaultheria procumbens*). It occurs in many different plants in the form of a glucoside (B. **29,** R. 511; C. 1899, II. 881).

When the methyl ester is digested with an alcoholic solution of potassium hydroxide and methyl iodide, we get the **dimethyl ester** $C_6H_4.\langle^{OCH_3}_{CO_2.CH_3}$, boiling at 245°. Boiled with potassium hydroxide, it is saponified, yielding methyl alcohol and methyl-salicylic acid $C_6H_4\langle^{O.CH_3}_{CO_2H}$, melting at 98°. It decomposes into carbon dioxide and anisol when heated to 200°.

The **chloride** $CH_3O[2]C_6H_4COCl$, b.p.$_{17}$ 145°, is obtained from the acid with thionyl chloride (C. 1902, II. 216).

Phenol-salicylic ester, *salol* $HO.C_6H_4.CO_2.C_6H_5$, melting at 43° and boiling at 172° (12 mm.), results on heating salicylic acid alone to 200°–220°, with the elimination of water and carbon dioxide; from salicylic acid, phenol, and $POCl_3$; from poly-salicylide on heating with phenol, or when phosgene acts upon the sodium salts of salicylic acid and phenol. It is applied as an antiseptic. It changes to *xanthone*, or diphenylene-ketone oxide, when it is heated. When *sodium salol* $C_6H_4(ONa).CO_2.CH_2H_5$ (from salol and sodium) is heated to 280°–300°, it changes to the isomeric sodium salt of **phenyl-salicylic acid** $C_6H_4(O.C_6H_5).CO_2H$, which melts at 113°, and is not coloured by ferric chloride. This acid is also obtained by heating o-chloro-benzoic acid with alkaline phenolates, in the presence of copper (B. **38,** 2111). **Phenyl-salicylic-acid-phenyl ester** $C_6H_5O[2]C_6H_4[1]COOC_6H_5$, m.p. 100°, is formed by heating phenyl-carboxylate $(C_6H_5O)_2CO$ with sodium carboxylate, CO_2, and phenol (C. 1903, I. 1362).

Acetyl-salicylic acid $CH_3CO.O.C_6H_4COOH$, m.p. 135°, is used as an anti-neuralgic, under the name *aspirin*. The anhydride, m.p. 85°, is formed from the acid with $SOCl_2$ or $COCl_2$ in pyridin solution (C. 1908, II. 996).

Carbo-methoxy-salicylic acid $CH_3OCO.O[2]C_6H_4[1]COOH$, m.p. 135° with decomposition, from salicylic acid, chloro-carbonic ester, and dimethyl-aniline (B. **42,** 218).

Salicyl-acetic acid $C_6H_4(OCH_2COOH)COOH$, m.p. 190°, is prepared by oxidising aldehydo-phenoxy-acetic acid, and from the sodium salts of several acid derivatives of salicylic acid with chloracetic ester and subsequent saponification. The esters of the acids are condensed by sodium to keto-cumarane-carboxylic esters (B. **33,** 1398; C. 1900, II. 461).

Salicyl chloride $HO.C_6H_4COCl$ is not known. It is true that PCl_5 acts very energetically upon salicylic acid, but the resulting phosphor-oxy-chloride is transposed by the phenol-hydroxyl, with evolution of hydrochloric acid:

$$C_6H_4\begin{cases}[1]COOH\\[2]OH\end{cases}\xrightarrow{PCl_5}C_6H_4\begin{cases}[1]COCl\\[2]OH\end{cases}\xrightarrow{POCl_3}C_6H_4\begin{cases}[1]COCl\\[2]OPOCl_2\end{cases},$$

and there results:

o-Chloro-carbonyl-phenyl-ortho-phosphoric-acid dichloride, melting at 168° (11 mm.). If the PCl_5 continues to act, this compound will exchange an oxygen atom for two chlorine atoms, and **o-trichloro-methyl-phenyl-ortho-phosphoric-acid dichloride** $(Cl_2PO)O[2]C_6H_4[1]CCl_3$, boiling at 178° (11 mm.), will be formed. When this is heated with PCl_5 in a sealed tube to 180°, there results :

o-Chloro-benzo-trichloride $Cl[2]C_6H_4[1]CCl_3$, melting at 30° and boiling at 130° (11 mm.) (A. **289,** 314). m- and p-Oxy-benzoic acids, as well as m- and p-cresotinic acids, behave similarly.

If, however, the hydrogen atom of the phenol-hydroxyl is replaced by the carbo-methoxyl or acetyl group, then PCl_5 produces the chlorides :

Methyl-salicyl chloride $CH_3O[2]C_6H_4[1]COCl$, boiling at 254°; **acetyl-salicyl chloride** $CH_3CO_2[2]C_6H_4[1]COCl$, melting at 43° and boiling at 135° (12 mm.) ; also **carbo-methoxy-salicylic chloride** $CH_3OCOO[2]C_6H_4[1]COCl$, b.p. 107°–110°.

When halogen atoms, nitro-groups, or methyl groups are introduced into salicylic acid, and then occupy the o-position with reference to the phenol-hydroxyl, the latter will be protected by them from the attack of the phosphorus oxy-chloride. Consequently, in the action of PCl_5 *free oxy-chlorides* will be produced :

o-Cresotinic chloride $HO[2]C_6H_3[3]CH_3[1]COCl$, melting at 28° ; **3-chloro-salicyl chloride,** melting at 63° ; **[3, 5]-dichloro-salicyl chloride,** melting at 79° ; and **[3, 5]-dichloro-nitro-salicyl chloride,** melting at 70° (B. **30,** 221) ; also the 3, 5-dibromo- and 3, 5-di-iodo-chlorides (A. **346,** 300).

The influence of substituents in the vicinity of the phenol-hydroxyl group is manifested in other ways, as in that of the esterification of [2, 6]-substituted benzoic acids with alcohol and hydrochloric acid.

Salicylo-phosphoric chloride $C_6H_4\begin{cases}[1]COO\\[2]O\end{cases}>PCl$, melting at 30° and boiling at 167° (11 mm.), is readily formed when PCl_3 acts upon salicylic acid at 70° (A. **289,** 301). All substituted salicylic acids react similarly (B. **30,** 221).

Salicylo-salicylic acid $HO[2]C_6H_4[1]COO[2]C_6H_4[1]COOH$, m.p. 148°, is formed by careful treatment of salicylic acid and its salts with $SOCl_2$, PCl_3, $COCl_2$, etc. It is used in medicine under the name *diplosal* (C. 1909, II. 1285).

Salicylides.—An intramolecular anhydride of salicylic acid of the formula $C_6H_4\begin{cases}CO\\O\end{cases}$ is unknown, but several polymers of this hypothetical simplest salicylide have been prepared :

Di-salicylide $C_6H_4\begin{cases}CO.O\\O.CO\end{cases}C_6H_4$, needles, m.p. 201°, produced by conducting phosgene into a pyridin solution of salicylic acid (B. **34,** 2951).

Tetra-salicylide $\begin{matrix}O\ .\ C_6H_4.COO.C_6H_4.CO\\ | \qquad\qquad\qquad\qquad\qquad\qquad |\\ CO.C_6H_4O.CO.C_6H_4O\end{matrix}$, m.p. 260°, and **poly-salicylide** $(C_7H_4O_2)_x$, m.p. 322°–325°, are produced when $POCl_3$ acts upon salicylic acid in xylol solution. The two compounds are separated by means of boiling chloroform, with which the tetra-salicylide forms a compound, **salicylide chloroform** $(C_7H_4O_2)_4.2CHCl_3$, crystallising in beautiful quadratic octahedra, which contain 33 per cent. of chloroform,

loosely combined as chloroform of crystallisation. This body has been used technically in the preparation of pure chloroform (Anschütz, A. **273,** 94). o-Cresotinic acid and the o-haloid-salicylic acids behave similarly (B. **35,** 3644). Concerning later molecular-weight determinations of tetra-salicylide, see A. **367,** 164.

Salicyl-amide $HO.C_6H_4.CONH_2$ melts at 138° (B. **24,** 138). If phosgene is allowed to act upon a pyridin solution of salicyl-amide, we obtain salicylic nitrile (see below) and **carbonyl-salicyl-amide** $C_6H_4\begin{cases}CO.NH\\O—CO\end{cases}$, m.p. 227°, which is more easily obtained from chloro-carbonic ester with salicyl-amide in pyridin (B. **35,** 3647). The O-acyl-salicylic amides are unstable, and, on fusing, or heating with pyridin, they easily pass into the isomeric N-acyl compounds:

$$AcOC_6H_4CONH_2 \longrightarrow HOC_6H_4CONHAc.$$

Under certain conditions this migration of the acyl residue is reversible (B. **40,** 3506). Bromine and alkali transpose salicyl-amide into carbonyl-amido-phenol, which is further brominated to dibromo-carbonyl-amido-phenol (C. 1900, I. 255).

Salicyl-anilide $C_6H_4(OH)CONHC_6H_5$ changes, when heated in dry condition, to *acridone* $C_6H_4\begin{cases}CO\\NH\end{cases}C_6H_4$. It is very probable that it is at first rearranged into phenyl-anthranilic acid (B. **29,** 1189). *Salicylo-nitrile* $HO.C_6H_4.CN$, m.p. 98°, is obtained from salicyl-aldoxime and acetic anhydride (B. **26,** 2621; **27,** R. 134; **31,** 3087).

Salicylic-acid hydrazide $HO.C_6H_4CONH.NH_2$, m.p. 147°, gives with HNO_2 **salicylic-acid azide** $HO.C_6H_4.CON_3$, m.p. 27°, crystals of a penetrating odour. **Salicyl-uric acid** $HO.C_6H_4CO.NHCH_2COOH$, m.p. 170°, occurs in urine after taking salicylic acid (A. **97,** 250); synthetically, it is prepared from salicylic-acid azide or carbo-methyoxy-salicylic-acid chloride and glycocoll (B. **42,** 219).

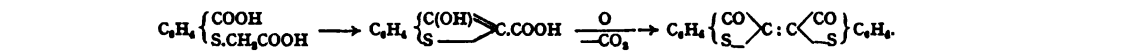
Thio-salicylic acid, and its derivatives, have lately acquired great industrial importance on account of their easy conversion into indigoid sulphur dyes; see Thio-indigo, and A. **351,** 390.

Thio-salicylic acid HS[2]C_6H_4[1]COOH, m.p. 164° (?), is formed (1) from diazotised anthranilic acid by transposition with potassium xanthogenate or sulpho-cyanate, or alkali polysulphides, and reduction of the resulting compounds: $CO_2HC_6H_4S.C.SOC_2H_5$, $CO_2HC_6H_4SCN$, $(CO_2HC_6H_4)_2S_2$; (2) from chloro-benzoic acid by heating with alkaline sulpho-hydrates or alkaline sulphides with addition of powdered copper (German patent 189,200); (3) by reduction from the unstable o-sulpho-benzoic dichloride. By oxidation, it is easily converted into **dithio-salicylic acid** $S_2(C_6H_4COOH)_2$, m.p. 289° (B. **31,** 1665).

Methyl-thio-salicylic acid $CH_3SC_6H_4COOH$, m.p. 169°, is formed by the action of dimethyl sulphate or methyl iodide upon alkaline solutions of thio-salicylic acid, di-thio-salicylic acid, o-rhodano-benzoic acid, etc. On melting with alkalies, with addition of a condensing agent like disodium cyanamide, sodium-lead, etc., it passes into thio-indoxyl (German patent 200,200).

Acetylene-bis-thio-salicylic acid $CO_2HC_6H_4S.CH:CH.SC_6H_4COOH$, formed by the action of acetylene dichloride upon the alkali salts of thio-salicylic acid. With an acid condenser it gives thio-indigo.

Phenyl-thio-glycol-o-carboxylic acid HOCO[1]C_6H_4[2]$S.CH_2COOH$, m.p. 213°, is obtained (1) from thio-salicylic acid and monochloracetic acid; (2) by the action of thio-glycollic acid upon o-diazo-benzoic acid. Its **nitrile,** m.p. 140°, is formed from o-amido-thio-phenol by transposition with monochloracetic acid, and replacement of the amido-group by the cyanogen group, through the diazo-compound (A. **351,** 412). On heating with alkali, the phenyl-thio-glycol-o-carboxylic acid and its nitrile pass into *thio-indoxyl-carboxylic acid,* which is easily converted into *thio-indigo* by splitting off CO_2 and oxidation:



Phenyl-thio-salicylic acid $C_6H_5SC_6H_4COOH$, m.p. 167°, from o-chloro-benzoic acid, sodium thio-phenol, and copper. Gives thioxanthone on warming with concentrated H_2SO_4 and acetic anhydride (A. **263,** 2; B. **37,** 4526; C. 1905, I. 1394). **Thio-salicylic-phenyl ester** $HSC_6H_4CO_2C_6H_5$, m.p. 91°, from thio-salicylic acid, phenol, and $POCl_3$ (B. **42,** 1134).

Diphenyl-sulphide-o, o-dicarboxylic acid $S(C_6H_4COOH)_2$, m.p. 230°, by heating thio-salicylic acid with o-chloro-benzoic acid and copper (B. **43,** 588).

Substituted Salicylic Acids.—The 5-derivatives of the mono-substitution products are the most readily prepared. 3-Derivatives are formed simultaneously. Of the di-substituted salicylic acids, the 3, 5-derivatives are most easily made. In them the substituents enter the o p-position, referred to phenol-hydroxyl. **5-Chloro-, 5-bromo-, 5-iodo-,** and **5-nitro-salicylic acids** melt at 172°, 164°, 196°, and 228° respectively.

5-Nitroso-salicylic acid, m.p. 156° with decomposition, blue-green crystals, from 5-nitroso-methyl-anthranilic acid on boiling with NaHO. It may be regarded as possible quinone-oxime-carboxylic acid (B. **42,** 2757).

3-Chloro-, 3-bromo-, 3-iodo-, and **3-nitro-salicylic acids** melt at 178°, 220°, 193°, and 144° respectively (B. **33,** 3240).

3-Nitro-salicylic acid is prepared synthetically from nitro-malone-aldehyde and aceto-acetic ester (C. 1900, II. 560).

3, 5-Dichloro-, 3, 5-dibromo-, 3, 5-di-iodo-, and **3, 5-dinitroso-salicylic acids** melt at 214°, 223°, 220°–230° with decomposition, and at 173° respectively. An **anhydride,** melting at 187° (B. **30,** 223), has been prepared by the action of the chloride of 3, 5-dichloro-salicylic acid upon the silver salt (B. **30,** 223; A. **346,** 307). For other halogen-substituted salicylic acids, see B. **38,** 3294.

3-Amido-salicylic acid NH_2[3]C_6H_3[2](OH)COOH, see *J. pr. Ch.* 2, **61,** 532. **5-Amido-salicylic acid** NH_2[5]C_6H_3[2](OH)COOH is formed by reduction of **benzol-azo-salicylic acid** $C_6H_5N_2C_6H_3(OH)COOH$ (C. 1906, II. 1058).

By diazotising, and successive combination with α-naphthyl-amine and with α-naphthol-sulphonic acid, diamond black is obtained; by reduction of the diazo-compound, **hydrazin-salicylic acid** $NH_2NHC_6H_3(OH)COOH$, m.p. 148° (B. **32,** 81; C. 1900, I. 205). **5-Diethyl-glycocoll-amido-salicylic methyl ester** $(C_2H_5)_2NCH_2CO.NH.C_6H_3(OH)COOCH_3$ is recommended as a local anæsthetic, and called *nirvanin.* **Sulpho-salicylic acid** $(SO_3H)C_6H_3(OH)COOH$, and **nitro-sulpho-salicylic**

acid, see B. **33,** 3238; *J. pr. Ch.* 2, **61,** 545. **Amido-sulpho-salicylic acid** is formed from nitro-salicylic acid with Na bisulphite (C. 1901, II. 716).

m-Oxy-benzoic acid $HO[1]C_6H_4[1]CO_2H$, m.p. 200°, sublimes without decomposition. **p-Oxy-benzoic acid** $HO[4]C_6H_4[1]CO_2H$ melts, when anhydrous, at 210° with partial decomposition into carbon dioxide and phenol. Its **methyl ester** melts at 131° and boils at 270°–280° (B. **27,** R. 570). The two acids are obtained from their corresponding amido- and haloid benzoic acids by methods 1 and 2. See above for the production of p-oxy-benzoic acid, together with salicylic acid, by methods 8 and 9. p-Oxy-benzoic acid is also obtained from many resins by fusing them with caustic potash. For the behaviour of m- and p-oxy-benzoic acids with PCl_5, consult above. Compare A. **261,** 236, for the action of chlorine upon the three oxy-benzoic acids.

m-Oxy-p-amido- and **m-amido-p-oxy-benzoic methyl ester,** m.p. 121° and 111°, are known as local anæsthetics, under the names *orthoform* and *new orthoform* (A. **311,** 26).

Anisic acid, *p-methoxy-benzoic acid* $CH_3O[4]C_6H_4[1]CO_2H$, m.p. 185° and b.p. 280°, is, like benzoic and salicylic acids, one of the acids which has been long known. It is isomeric with methyl-salicylic ester and the other monomethyl derivatives of the oxy-benzoic acids in general, as well as with the oxy-phenyl-acetic acids. Anisic acid is easily obtained, hence numerous transposition products of it are known. It is prepared by oxidising *anethol,* the chief ingredient of anise oil, and other ethereal oils containing anethol (*q.v.*), with dilute nitric acid, or with a chromic acid mixture. Synthetically, it is obtained from p-bromo-anisol, Mg, and CO_2 (C. 1903, I. 636).

Nitrile, m.p. 60°, b.p. 257°, from p-nitro-benzo-nitrile with sodium methylate. Also from anisamide with PCl_5, and from anisol, BrCN, and $AlCl_3$ (B. **33,** 1056; **36,** 648; C. 1900, I. 130).

History.—Cahours (1839) discovered anisic acid when he oxidised anise oil (A. **41,** 66). Kolbe at first considered it methoxy-benzoic acid, because when it was distilled with caustic baryta it broke down into CO_2 and *anisol.* Saytzew (1863) found that when anisic acid was heated with hydriodic acid it yielded an acid different from salicylic acid, yet isomeric with the latter (A. **127,** 129). This was subsequently found to be p-oxy-benzoic acid. In 1867 Ladenburg showed that anisic acid could be prepared by saponifying the dimethyl ether ester of p-oxy-benzoic acid (A. **141,** 241).

Oxy-toluic Acids or **Cresotinic Acids** $CH_3.C_6H_3(OH).CO_2H$.—The ten possible isomerides are known (B. **16,** 1966). They are isomeric with the three oxy-methyl-benzoic acids, or benzyl-alcohol-carboxylic acids, and phenyl-glycollic acid, or almond acid. They have been prepared from the toluic acids by methods 1 and 2, from the oxy-aldehydes by method 6, and from the cresols by methods 8 and 9.

Homo-salicylic acids:

$CH_3[3]C_6H_3[2, 1](OH)COOH$, m.p. 163°.
$CH_3[4]C_6H_3[2, 1](OH)COOH$, „ 177°.
$CH_3[5]C_6H_3[2, 1](OH)COOH$, „ 151°.
$CH_3[6]C_6H_3[2, 1](OH)COOH$, „ 168°.

Methyl-m-oxy-benzoic acids:

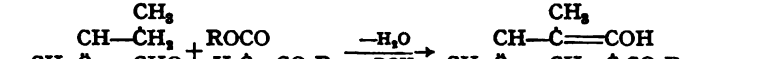
$CH_3[2]C_6H_3[3, 1](OH)COOH$, m.p. 183°.
$CH_3[4]C_6H_3[3, 1](OH)COOH$, „ 206°.
$CH_3[5]C_6H_3[3, 1](OH)COOH$, „ 208°.
$CH_3[6]C_6H_3[3, 1](OH)COOH$, „ 184°.

Methyl-p-oxy-benzoic acids:

$CH_3[2]C_6H_3[4, 1](OH)COOH$, m.p. 177°.
$CH_3[3]C_6H_3[4, 1](OH)COOH$, m.p. 172°.

Those isomerides, containing the hydroxyl group in the ortho-position with reference to carboxyl, are coloured violet by ferric chloride, just like salicylic acid. They dissolve easily in cold chloroform and are volatile with steam. See above for their behaviour towards PCl_5, PCl_3, $POCl_3$, etc. *3-Methyl-homo-salicylic acid* yields an *o-homo-salicylic* or *o-cresotide chloroform* (A. **273,** 88) similar to *salicylide chloroform.* 5-Methyl-m-oxy-benzoic acid, prepared synthetically by the action of baryta water upon acetone-oxalic ester (B. **22,** 3271), yields by nitration *nitrococcic acid* or *2, 4, 6-trinitro-m-oxy-m-toluic acid,* melting at 180°, which is also formed when carminic acid, the dye of red cochineal, is oxidised (B. **26,** 2648). The 6-methyl-m-oxy-benzoic acid is best obtained by heating β-naphthol-6, 8-disulphonic acid with 50 per cent. NaHO to 260°–280° (A. **350,** 253). When the three isomeric cresotinic acids, or, better, their dibromo-substitution products, are reduced with sodium and amyl alcohol, the ring is ruptured and α-, β-, and γ-methyl-pimelic acids are produced (A. **295,** 173).

o- and **p-Oxy-mesitylenic acids** $HO.C_6H_2(CH_3)_2CO_2H$ melt at 179° and 223° (A. **206,** 197; **311,** 372). The former is obtained by nuclear synthesis, through condensation of α-methyl-β-ethyl-acroleïn with malonic ester, and treatment of the product with sodium alcoholate (A. **358,** 71) :



Similarly, we obtain from citral (*q.v.*) and malonic ester **8-iso-amenyl-4-methyl-salicylic acid,** m.p. 167°.

The **trimethyl-oxy-benzoic acids** (B. **21,** 884), as well as **ethyl-methyl-oxy-benzoic acids** (A. **195,** 284), are also known. The corresponding iso-propyl-oxy-benzoic acids—**thymo-** and **iso-oxy-cumic acids,** melting at 142° and 94° (B. **19,** 3307)—result upon fusing carvacrol and thymol with caustic potash.

Different isomeric p-methyl-iso-propyl-oxy-benzoic acids $(CH_3)(C_3H_7)C_6H_2(OH)COOH$: **thymotic** and **carva-crotinic acids** have been made by introducing the CO_2 group into thymol and carvacrol. See B. **28,** 2795, for the derivatives of thymotic acid.

The *oxy-phenyl-fatty acids* attach themselves to the alkyl-substituted oxy-benzoic acids. They are produced (1) by diazotising the corresponding amido-phenyl-fatty acids, and then decomposing the diazo-derivatives with boiling water; (2) by saponifying the oxy-benzyl cyanides.

The o-oxy-acids, in which the phenol-hydroxyl group occupies the γ- or δ-position with reference to the carboxyl group, are, in contrast to the corresponding o-amido-fatty acids, capable of existing, but when heated they part with water and yield γ- and δ-lactones (Vol. I.).

The **oxy-phenyl-acetic acids** $HO.C_6H_4.CH_2.CO_2H$ are isomeric with the ten oxy-toluic acids (see these), with the three oxy-methyl-benzoic acids, and with the mandelic acids. o-Oxy-phenyl-acetic acid, bearing close relationship to oxindol and isatin (*q.v.*), is also obtained from o-oxy-mandelic acid by reduction with hydriodic acid. Ferric chloride colours it violet. It passes into its lactone (see below) when it is heated. *p-Oxy-phenyl-acetic acid* occurs in urine, and arises from the

decomposition of albuminous bodies as well as in that of *sinalbin*, occurring in the seeds of white mustard (B. **22**, 2137).

o-, m-, and **p-Oxy-phenyl-acetic acids** melt at 137°, 129°, and 148°. **m-** and **p-Oxy-phenyl-aceto-nitrile** melt at 52° and 69° (B. **22**, 2139).

5, 2-Nitro-oxy-phenyl-acetic acid, m.p. 149°, is obtained, synthetically, by condensation of nitro-malonic aldehyde and lævulinic acid (C. 1900, II. 560).

Oxy-phenyl-propionic acids.—Four of the six theoretically possible acids are known.

Phloretic acid, *p-oxy-hydratropic acid* $HO[4]C_6H_4[1]CH\langle^{CO_2H}_{CH_3}$, melting at 129°, is formed, together with phloro-glucin, when phloretin (the phloro-glucin ester of phloretic acid) is digested with potassium hydroxide. It has been prepared synthetically from p-amido-hydro-cinnamic acid. Ferric chloride colours its solution green. Baryta decomposes it into ethyl-phenol; fusion with potassium hydroxide produces para-oxy-benzoic acid.

Phloretin, *monophloretic phloro-glucin ester* $(HO)_2C_6H_3O.CO.CH(CH_3).C_6H_4OH$, melts at 254° (B. **27**, 1631, 2686). See Phlorizin.

Hydro-cumaric acids or **β-phenol-propionic acids** $HO.C_6H_4.CH_2.CH_2.CO_2H$ result when the corresponding cumaric acids, the oxy-cinnamic acids, or β-oxy-phenyl-acrylic acids are reduced with sodium amalgam.

o-Hydro-cumaric acid or *melilotic acid*, melting at 81°, occurs free and in combination with cumarin, the lactone of o-oxy-cinnamic acid, in the yellow melilot (*Melilotus officinalis*). It is produced by the action of sodium amalgam upon cumarin. Ferric chloride imparts a bluish colour to the solution. When distilled, it passes into its lactone —hydro-cumarin. It yields salicylic acid when it is fused with caustic potash.

m- and **p-Hydro-cumaric acids** melt at 111° and 128°. p-Hydro-cumaric acid is also produced in the decomposition of tyrosine.

γ- and δ-**Lactones** of o-oxy-phenyl-fatty acids are produced when these acids are distilled. They correspond to the γ- and δ-lactames described above.

o-Oxy-phenyl-acetic acid lactone $C_6H_4\{^{[1]CH_2.CO}_{[2]O\text{——}|}$ melts at 49° and boils at 236° (B. **17**, 975).

Hydro-cumarin, β-o-Oxy-phenyl-propionic acid lactone $C_6H_4\{^{[1]CH_2.CH_2.CO}_{[2]O\text{————}|}$, melts at 25° and boils at 272°. When boiled with water it regenerates the acid from which it was produced by distillation.

B. **Dioxy-monocarboxylic Acids** are obtained by the same methods which were used in the preparation of the aromatic monocarboxylic acids. The carboxyl group is more readily introduced into the dioxy-benzols than into the monoxy-benzols. This occurs upon heating the bodies with a solution of ammonium or sodium carbonate to 100° or 130° (B. **18**, 3202; **19**, 2318; A. **851**, 313). The dioxy-benzoic acids break down, when heated, into carbon dioxide and dioxy-benzols.

Dioxy-benzoic Acids.—The six possible isomerides are known. The most important member of this class is :

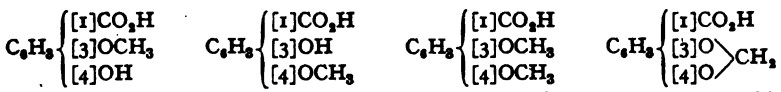
Proto-catechuic acid, 3, 4-*dioxy-benzoic acid* $(HO)_2[3,4]C_6H_3[1]CO_2H + H_2O$, in yellow needles, melts, when anhydrous, at 190°, and decomposes into pyro-catechin and carbonic acid. It occurs in the fruit of *Illicium religiosum*. It has been obtained from many tri-derivatives of benzene, containing substituents in the 3, 4-position with reference to a side chain, by fusing them with caustic potash—*e.g.* from the corresponding bromo- and iodo-p-oxy-benzoic acids, bromanisic acid, p- and m-cresol-sulphonic acid, sulpho-p- and sulpho-m-oxy-benzoic acids, from eugenol, piperic acid (compare also piperonylic acid), etc., as well as from various resins (benzoïn, asafœtida, myrrh, and, particularly, kino) on fusion with potassium or sodium hydroxide. The latter resin readily yields large quantities of the acid (A. **177,** 188). Compare further phloro-glucin ethers of pyro-catechuic acid. It is also produced by the action of bromine upon quinic acid in aqueous solution.

The *two* possible pyro-catechuic monocarboxylic acids are produced when pyro-catechin is heated to 140° with a solution of ammonium carbonate.

Ferric chloride colours the solution green; after the addition of a very dilute soda solution it becomes blue, later red (all derivatives containing the proto-catechuic residue $(OH)_2C_6H_3.C$ (B. **14,** 958) react similarly). Ferrous salts colour its salt-solutions violet. It reduces an ammoniacal silver solution, but not an alkaline copper solution. **Diproto-catechuic acid** $C_{14}H_{10}O_7$, is a tannic acid which results on boiling proto-catechuic acid with aqueous arsenic acid. It is very similar to common tannic acid, but is coloured green by ferric oxide. It forms a compound with p-oxy-benzoic acid by the union of equimolecular quantities (A. **134,** 276; **280,** 18).

See Naphthalene ring formations for the conversion of substituted proto-catechuic acids, by oxidation with nitric acid, into derivatives of β-naphtha-quinone.

The phenol ethers of proto-catechuic acid are:



Vanillic acid — Iso-vanillic acid — Veratric acid — Piperonylic acid.

These alkyl-and alkylene-ether acids are formed when proto-catechuic acid is treated with CH_3I, CH_2I_2, and $CH_2Br.CH_2Br$ and caustic potash, as well as by oxidising the corresponding ethers of proto-catechuic aldehyde. The proto-catechuic acid can be regained from them upon heating with hydrochloric acid to 150°, when the dimethyl-ether acid will yield at first the two monomethyl-ether acids; whereas the methylene ether, piperonylic acid, separates carbon in addition to proto-catechuic acid:

$$CO_2H.C_6H_3\langle{}^{O}_{O}\rangle CH_2 = CO_2H.C_6H_3\langle{}^{OH}_{OH} + C.$$

The alkyl-ether acids break down into carbon dioxide and alkyl-pyro-catechuic ethers when they are heated with lime or baryta.

Vanillic acid, *m-methyl-proto-catechuic acid,* melting at 211°, sublimes. It is obtained by the energetic oxidation of its aldehyde, vanillin, also from coniferin, as well as by the decomposition of *aceto-vanillic acid,*

melting at 142°, the oxidation product of aceto-eugenol, aceto-ferulic acid, and aceto-homo-vanillic acid, when they are treated with potassium permanganate. Its *nitrile* melts at 87° (B. **24,** 3654).

Iso-vanillic acid, *p-methyl-proto-catechuic acid*, melts at 250°, and was first obtained from hemi-pinic acid (see this), or 4, 5-dimethoxy-o-phthalic acid upon heating with hydrochloric acid.

Veratric acid, 3, 4-*dimethoxy-benzoic acid*, melting at 179·5°, occurs, together with *veratrin* (see the alkaloids), in the sabadilla seeds (from *Veratrum Sabadilla*).

Diethyl-proto-catechuic acid melts at 149°.

Piperonylic acid, *methylene-proto-catechuic acid*, melting at 228°, is also formed by oxidising *a*-homo-piperonylic acid, obtained from safrol, as well as from piperonal and proto-catechuic acid (see this). It breaks down when heated with hydrochloric acid (see above). By the action of PCl_5, and subsequent treatment with cold water, it can be converted into the carboxylate of proto-catechuic acid, and into the latter itself by saponification (C. 1908, I. 1689). Its *nitrile* melts at 95° (B. **24,** 3656).

Ethylene-proto-catechuic acid melts at 133°.

The *phloro-glucin ethers of proto-catechuic acid* are probably certain vegetable substances which, upon fusion with caustic potash, break down into phloro-glucin and proto-catechuic acid. They are also related to the *flavones* (*q.v.*), belonging to the pyrone group. They are:

Luteolin $C_{15}H_{10}O_6$ (B. **29,** R. 647, 848), occurs in *Reseda luteola* and crystallises in yellow needles. Ferric chloride colours it green.

Catechin, from catechu, and **Maclurin** or **moringa tannic acid** $C_{13}H_{10}O_6+H_2O$, from yellow wood, *Morus tinctoria*, are generally included among the tannic acids. *Proteaic acid* $C_9H_{10}O_4$ appears to be a homologue of proto-catechuic acid. It is present in *Protea mellifera* (B. **29,** R. 415).

Pyro-catechin-o-carboxylic acid, 2, 3-*dioxy-benzoic acid* $(HO)_2C_6H_3CO_2H+2H_2O$, melts at 199° when anhydrous. It readily breaks down into CO_2 and pyro-catechin, from which it is formed, together with proto-catechuic acid, by the action of ammonium carbonate (A. **220,** 116). It also results when 3-iodo-salicylic acid is fused with caustic potash.

Resorcinol-monocarboxylic Acids.—There are three. Sym. dioxy-benzoic acid results on heating sym. disulpho-benzoic acid with caustic potash, and the other two acids are produced when resorcinol is treated with ammonium dicarbonate or potassium dicarbonate solution (B. **18,** 1985; **18,** 2379).

The *a*-compound is not coloured by ferric chloride; whereas the *β*-body is coloured a dark red, and the *γ*-modification blue-violet, by the same reagent.

***a*-Resorcylic acid,** 3, 5-*dioxy-benzoic acid* $(HO)_2C_6H_3CO_2H+1\frac{1}{2}H_2O$, melts at 233°. It yields *anthrachrysone* (*q.v.*) when it is heated with sulphuric acid.

***β*-Resorcylic acid,** 2, 4-*dioxy-benzoic acid* $+3H_2O$, melts in the anhydrous state at 213°. See B. **28,** R. 1051; **29,** R. 30, for the ethers and esters of the acid.

It is converted in glacial acetic acid solution by chlorine into hexachloro-m-diketo-hexene (B. **25,** 2687). The *nitrile* melts at 175°.

γ-Resorcylic acid, 2, 6-*dioxy-benzoic acid*, melts at 148°–167°, and breaks down into CO_2 and resorcinol.

Gentisinic acid, **hydroquinone-carboxylic acid,** 2, 5-*dioxy-benzoic acid*, melts at 200°, and at 215° breaks down into carbon dioxide and hydroquinone. It was first prepared from gentisin, a xanthone derivative, together with phloro-glucin, on fusing it with caustic potash. It is obtained from 5-bromo-, 5-iodo- and 5-amido-salicylic acids; also from hydroquinone and from gentisinic aldehyde (B. **14,** 1988). It is most easily obtained by oxidation of salicylic acid with potassium persulphate in alkaline solution (A. **840,** 213). Ferric chloride colours it a deep blue and is decomposed into CO_2 and quinone (B. **18,** 3499).

The **Dioxy-toluic Acids** $(HO)_2C_6H_2(CH_3)CO_2H$ are isomeric with the dioxy-phenyl-acetic acids. The most important of the known acids of this class is *orsellinic acid*, 2, 6-dioxy-p-toluic acid, which melts at 176° and breaks down into CO_2 and orcin. It is obtained from orsellic acid upon boiling the latter with water, or from erythrin with baryta water. It is coloured violet by ferric chloride.

Orsellic acid, *diorsellinic acid* or *lecanoric acid* $C_{16}H_{14}O_7$, melting at 153°, is an ether-like anhydride of orsellinic acid $(HO)_2.C_6H_2(CH_3).CO.OC_6H_2(OH)(CH_3)CO_2H$ (?). It is found in different mosses of the varieties *Roccella* and *Lecanora*. Boiling water converts it into orsellinic acid.

Erythrin $C_{20}H_{22}O_{10}+1\frac{1}{2}H_2O$, *erythrinic acid*, is an ether derivative of diorsellinic acid and erythrite. It occurs in the lichen *Roccella fuciformis*, which is applied in the manufacture of archil, and is extracted from it by means of milk of lime. When it is boiled with water it breaks up into orsellinic acid and—

Picro-erythrin $C_{12}H_{16}O_7+H_2O$, which, boiled with baryta water, yields erythrite, orcin, and carbon dioxide:

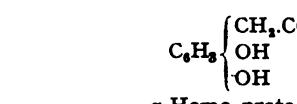
$$\text{Erythrin } C_{20}H_{22}O_{10}+H_2O = (HO)_2C_6H_2(CH_3)CO_2H+C_{12}H_{16}O_7$$
$$C_{12}H_{16}O_7+H_2O = (HO)_2C_6H_3CH_3+CO_2+C_4H_6(OH)_4 \text{ Erythrite.}$$

Everninic acid $C_9H_{10}O_4=(HO)_2C_6H(CH_3)_2CO_2H$ (?) is produced, together with orsellinic acid, on boiling *evernic acid* (from *Evernia prunastris*) with baryta. It melts at 157°, and is coloured violet by ferric chloride.

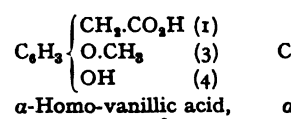
Dioxy-durylic acid, pseudo-cumene-hydroquinone-carboxylic acid $(HO)_2[2, 5]C_6[3, 4, 6](CH_3)_3CO_2H$, melts at 210° when rapidly heated, and results from the reduction of *durylic acid quinone*, pseudo-cumene-quinone-carboxylic acid $O_2[2, 5]C_6[3, 4, 6](CH_3)_3CO_2H$, which decomposes at 130°, and is obtained by the action of ferric chloride upon a hydrochloric acid solution of diamido-phenylic acid (A. **237,** 11).

Dioxy-phenyl-fatty Acids.—Certain dioxy-phenyl-acetic acids and dioxy-phenyl-propionic acids in this group are interesting.

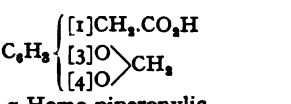
α-Homo-proto-catechuic acid and its ether acids have their side groups occupying the same positions as those of proto-catechuic acid and its ether acids:



α-Homo-proto-catechuic acid, m.p. 127°



α-Homo-vanillic acid, m.p. 142°



α-Homo-piperonylic acid, m.p. 127°.

The aceto-α-homo-vanillic acid and α-homo-piperonylic acid result in the moderated oxidation of aceto-eugenol (*q.v.*) and safrol (*q.v.*) with $KMnO_4$. The former melts at 140°, and is converted by caustic soda into α-homo-vanillic acid, which hydrochloric acid, at 180°, changes to α-homo-proto-catechuic acid (B. **10,** 207 ; **24,** 2882).

α-Homo-vanillic acid and α-homo-piperonylic acid have also been obtained from the condensation products of vanillin and piperonal with hippuric acid, by transformation into the corresponding pyro-racemic acids and oxidation with H_2O_2 (A. **370,** 372). α-Homo-proto-catechuic acid is best prepared from the cyano-hydrin of methyl-vanillin by boiling with HI (B. **42,** 2949).

Homo-veratric acid $(CH_3O)_2[3, 4]C_6H_3[1]CH_2COOH$, m.p. 99°.

2, 5-Dioxy-phenyl-acetic acid, *homo-gentisinic acid*, m.p. 147°, is found in human urine during alcaptonuria. It crystallises with one molecule H_2O, and has been synthesised from the corresponding dimethoxy-phenyl-aceto-nitrile, and from 2, 5-dioxy-mandelic acid by boiling with HI (C. 1907, II. 901).

Sym. dioxy-phenyl-acetic acid $(HO)_2[3, 5]C_6H_3[1]CH_2.CO_2H+H_2O$ melts at 54°.

The triethyl ester, obtained from the dicarboxylic acid derived from this acid, is produced by the condensation of acetone-dicarboxylic ester with sodium. It melts at 98°, and yields dioxy-phenyl-acetic acid upon saponification. It yields orcin when its silver salt is heated.

Hydro-caffeic acid, or β-3, 4-*dioxy-phenyl-propionic acid*, corresponds, like α-homo-proto-catechuic acid, in the same arrangement of the substituting groups, to proto-catechuic acid :

C_6H_3 { [1]$CH_2CH_2CO_2H$ [3]OCH_3 [4]OCH_3	C_6H_3 { [1]$CH_2CH_2CO_2H$ [3]OCH_3 [4]OH	C_6H_3 { [1]$CH_2CH_2CO_2H$ [3]OH [4]OCH_3	C_6H_3 { [1]$CH_2CH_2CO_2H$ [3]O [4]O$>CH_2$
Hydro-caffeic dimethyl-ether acid, m.p. 96°	Hydro-ferulic acid, m.p. 89°	Hydro-iso-ferulic acid, m.p. 164°	Hydro-caffeic methylene-ether acid, m.p. 81°.

Hydro-caffeïc acid itself, and its ether acids, are formed from the corresponding [3, 4]-dioxy-cinnamic or caffeïc acid, and their derivatives—ferulic and iso-ferulic acids—by reduction with sodium amalgam (B. **11,** 650 ; **13,** 758). The methylene-ether acid is also produced by oxidising β-hydro-piperic acid (*q.v.*) (B. **20,** 421). Ferric chloride colours hydro-caffeïc acid the same as it does proto-catechuic acid.

Hydro-umbellic acid, β-2, 4-*dioxy-phenyl-propionic acid* $(HO)_2[2, 4]C_6H_3.CH_2.CH_2.CO_2H$, decomposes at 110°. It is obtained from umbelliferone, the δ-lactone of [2, 4]-dioxy-cinnamic acid, by the action of sodium amalgam. Ferric chloride colours it green.

Hydroquinone-propionic acid $(HO)_2[2, 5]C_6H_3CH_2CH_2CO_2H$; its lactone melts at 163° ; obtained by oxidation of o-hydro-cumaric acid with potassium persulphate in alkaline solution (C. 1907, II. 901).

Trioxy-benzoic acids $(HO)_3C_6H_2CO_2H$. Three of the six possible isomerides are known. The most important is—

Gallic acid $(HO)_3[3, 4, 5]C_6H_2CO_2H+H_2O$. It melts and decomposes about 220° into CO_2 and *pyrogallol*. It occurs, free, in tea, in the fruit of *Cæsalpina coriaria* (*Divi-divi*), in mangoes, and in various other plants. It is obtained from the ordinary tannic acid (tannin) by boiling it with dilute acids. It is prepared artificially from bromo-

o-m-dioxy-benzoic acid and bromo-proto-catechuic acid when fused with potassium hydroxide.

Gallic acid crystallises in fine, silky needles. It dissolves with difficulty in cold water, but readily in hot water, alcohol, and ether. It has a faintly acid, astringent taste. It reduces both gold and silver salts (hence its application in photography). Ferric chloride throws down a blackish-blue precipitate in its solutions.

The solutions of its alkali salts absorb oxygen when exposed to the air, and, in consequence, become brown in colour.

Rufigallic acid, a derivative of anthracene (*q.v.*), is obtained by heating gallic acid with sulphuric acid.

Oxidising agents, such as arsenic acid and iodine, convert gallic into **ellagic acid,** probably a dilactone of a hexaoxy-diphenyl-dicarboxylic acid $\overset{CO.C_6H(OH)_2.O}{O—C_6H(OH)_2.CO}$ (M. **29,** 263). It is easily obtained in the oxidation of tannin with H_2O_2 besides the so-called *luteic acid*, the *monolactone* $\overset{CO.C_6H(OH)_3}{O—C_6H(OH)_2CO_2H}$, corresponding to ellagic acid. On distillation with zinc dust, ellagic acid yields fluorene (*q.v.*).

In alkaline solution gallic acid is converted into *galloflavin* (*q.v.*), a yellow dye of the xanthone group. Hydrochloric acid and potassium chlorate decompose the acid into iso-trichloro-glyceric acid or trichloro-pyro-racemic acid (Vol. I.).

Basic bismuth gallate $(HO)_3C_6H_2CO_2Bi(OH)_2$, under the name *dermatol*, is applied as an odourless drying antiseptic.

Basic bismuth oxy-iodide gallate $(HO)_3C_6H_2CO_2Bi(OH)I$ is used as a substitute for iodoform under the name of Airol.

Ethyl-gallic ester $(HO)_3C_6H_2CO_2C_2H_5$ melts at 141° when anhydrous. **Trimethyl-** and **triethyl-gallic-ether acids** $(R'O)_3C_6H_2\ CO_2H$ melt at 168° and 112°. The trimethyl-ether acid, heated with HCl, yields **3, 5-dimethyl-gallo-etheric acid** HO[4]$(CH_3O)_2$[3, 5]C_6H_2COOH, m.p. 202°, identical with syringa acid and also obtained from sinapinic acid or oxy-dimethoxy-cinnamic acid by oxidation. 4-Methyl-gallo-etheric acid, m.p. 240°, from gallic acid with dimethyl sulphate (B. **36,** 215, 660).

Methylene-methyl-gallic-ether acid, myristicinic acid $(CH_3O)(CH_2O_2)$. $C_6H_2CO_2H$ melts at 130°–135° (B. **24,** 3821) when it is anhydrous. **Triacetyl-gallic acid** melts with decomposition at 170°. **Gallic-acid anilide,** *gallanol*, has been used in medicine. This is true also of **dibromo-gallic acid,** or *gallo-bromol*, melting at 140°.

Pyrogallol-carboxylic acid $(HO)_3$[2, 3, 4]$—C_6H_2CO_2H+\frac{1}{2}H_2O$ is prepared by heating pyrogallol with potassium bicarbonate (B. **18,** 3205). It decomposes at 195°–200°, but sublimes without decomposition in a current of carbon dioxide. Ferric chloride colours it violet. **Triethyl-pyrogallol-carboxylic acid** $C_6H_2(O.C_2H_5)_3.CO_2H$ melts at 105°. It results in the oxidation of triethyl-daphnetic acid (*q.v.*).

Phloro-glucin-carboxylic acid $(HO)_3$[2, 4, 6]$C_6H_2CO_2H+H_2O$ decomposes even at 100°, also when boiled with water, into carbon dioxide and phloro-glucin, from which it is obtained by boiling with a potassium carbonate solution (B. **18,** 1323). For ethers of phloro-glucin-carboxylic acid, see C. 1903, I. 966.

An **oxy-hydroquinone-carboxylic acid** $(OH)_3$[1, 2, 4]C_6H_2COOH, m.p.

217°–218° with decomposition, is formed from oxy-hydroquinone on boiling with bicarbonate solution and passing CO_2 (B. **34,** 2840).

Triethyl-oxy-hydroquinone-ether acid $(C_2H_5O)_3[2, 4, 5]C_6H_2CO_2H$, m.p. 134°, results upon treating α- or β-æsculetine-triethyl-ether acid with potassium permanganate (B. **16,** 2113). **Trimethyl-oxy-hydroquinone-ether acid, asaronic acid,** m.p. 144°, is formed by the oxidation of the synthetic asaryl-aldehyde (B. **12,** 290).

Iridic acid, *α-homo-dimethyl-gallic-ether acid* $(CH_3O)_2(HO)[3, 4, 5]C_6H_2CH_2CO_2H$, m.p. 118°, is produced, along with formic acid and iretol, when irigenin is decomposed with baryta water (B. **26,** 2015).

Trimethyl-homogallic acid, *methyl-iridic acid* $(CH_3O)_3[3, 4, 5]C_6H_2.CH_2COOH$, m.p. 120°, is formed by the oxidation of elemicin (*q.v.*), and, synthetically, from trimethyl-gallic aldehyde (B. **41,** 3662).

Addendum: **Tannic Acids.**—The tannins, or tannic acids, are substances widely disseminated in the vegetable kingdom. They are soluble in water, possess an acid, astringent taste, are coloured dark blue or green (ink) by ferrous salts, precipitate gelatine, and enter into combination (leather) with animal hides. Hence they are employed in the manufacture of leather, and for the preparation of ink. They are precipitated from their aqueous solutions by neutral acetate of lead.

Some tannic acids appear to be glucosides of gallic acid—*i.e.* ethereal compounds of the same with various sugars or of their dehydration products. They decompose into gallic acid and grape sugar upon boiling with dilute acids. Others contain phloro-glucin instead of grape sugar. On fusing with KHO the tannic acids mostly form protocatechuic acid and phloro-glucin. For the constitution of the tannic acids, still somewhat obscure, see C. 1899, I. 559.

Gallo-tannic acid, tannin, occurs in large quantity (upward of 50 per cent.), in gall-nuts (pathological concretions upon different oak species, *Quercus infectoria,* produced by the sting of insects); it also occurs in sumach (*Rhus coriaria*), in tea, and in other plants.

Tannin is best obtained from gall-nuts. The latter are finely divided, and extracted with ether and alcohol. The solution separates into two layers, the lower of which is aqueous, and contains tannin chiefly, and this is obtained by evaporation. For further purification the solution, in amyl alcohol and ether, is fractionally precipitated with benzine (B. **31,** 3169).

Pure tannic acid is a colourless, shining, amorphous mass, very soluble in water, slightly in alcohol, and almost insoluble in ether. Many salts—*e.g.* sodium chloride—precipitate it from its aqueous solutions, and it can also be removed from the latter by shaking with acetic ether. It reacts acid, and is coloured dark blue by ferric chloride (ink); gelatine precipitates it. Quantitative methods of estimating tannin are based on this behaviour. Ordinary tannin is optically active, its coefficient of rotation being about +60°, but it is not uniform, since a more strongly marked constituent can be separated out, with a coefficient of about 76°. Tannin appears to consist of a mixture of *inactive digallic acid* $(HO)_3C_6H_2CO.OC_6H_2(OH)_2COOH$ and its reduction product, the *optically active leuco-tannin* $(HO)_3C_6H_2CH(OH).OC_6H_2(OH)_2COOH$, but this is contradicted by the very slight electric conductivity of tannin, and its apparently very high molecular weight

(B. **43,** 628). Dilute acids and alkalies split it up neatly into gallic acid, which is oxidised to ellagic acid and luteic acid by boiling in H_2O_2. Distillation with zinc dust produces diphenyl-methane.

Digallic acid (see above) crystallises with $2H_2O$, melts anhydrous at 268° to 270° with decomposition, and can be obtained from tannin by way of the carbethoxy-derivative. The acid behaves like tannin towards glue, $FeCl_3$, hydrolysis, and oxidation with H_2O_2. Its penta-acetate, m.p. 211° to 214°, yields, on reduction with zinc dust and glacial acetic acid, **hexa-acetyl-leuco-tannin,** m.p. 154°, which has also been isolated from the acetylation products of tannin.

We must distinguish the digallic acid obtained from tannin from the digallic acids $C_{14}H_{10}O_9$ obtained artificially from gallic acid with $POCl_3$, or arsenic acid. These were formerly believed to be identical with tannin, but they are distinguished from the latter by their much greater electrical conductivity and by their inability to become coagulated with arsenic acid (B. **31,** 3167).

The **penta-acetate** $C_{14}O_5(C_2H_3O)_5O_9$, heated to 210°, decomposes with formation of pyrogallol.

Gallyl-gallic acid $C_{14}H_{10}O_9$, a keto-tannic acid, forms an oxime and phenyl-hydrazone. See B. **22,** R. 754; **23,** R. 24.

The other tannic acids found in plants have been but little investigated; but we may mention—

Kino-tannin, which constitutes the chief ingredient of kino, the dried juice of *Pterocarpus erinaceus* and *Coccoloba uvifera.* Its solution is coloured green by ferric salts. It yields phloro-glucin on fusion with potassium hydroxide.

Catechu-tannin occurs in catechin, the extract of *Mimosa catechu.* Ferric salts colour it a dirty green. *Catechin* or *catechinic acid* $C_{21}H_{20}O_9 + 5H_2O$ is also present in catechu. It crystallises in shining needles.

Moringa-tannin $C_{13}H_{10}O_6 + H_2O$, *Maclurin,* is found in yellow wood (*Morus tinctoria*), from which it may be extracted (along with morin) with hot water. When the solution cools morin separates out; maclurin is precipitated from the concentrated liquid by hydrochloric acid, in the form of a yellow crystalline powder, soluble in water and alcohol. Ferric salts impart a greenish-black colour to its solutions. When fused with caustic potash it yields proto-catechuic acid and phloro-glucin. It forms pentacidyl derivatives (C. 1897, 466).

Morin $C_{13}H_8O_6 + 2H_2O$ decomposes into phloro-glucin and resorcin. Nitric acid oxidises it to β-resorcylic acid. Consult B. **29,** R. 646, for its constitution.

The *tannin* of *coffee* $C_{30}H_{18}O_{16}$ occurs in coffee beans and Paraguay tea. Gelatine does not precipitate its solutions. Ferric chloride gives them a green colour. It decomposes into caffeïc acid and sugar when boiled with potassium hydroxide. Proto-catechuic acid is produced when it is fused with potassium hydroxide.

The *tannin* of *oak* is found in the bark (together with gallic acid, ellagic acid, quercite). It has the formula $C_{19}H_{16}O_{10}$, and is a red powder, not very soluble in cold water, but more readily in acetic ether. Ferric chloride colours its solution dark blue. Boiling, dilute sulphuric acid converts it into the so-called *oak-red* (phlobaphene), $C_{28}H_{26}O_{17}$(?).

The *tannin* found in the quinine barks is combined with the quinia-alkaloids. It closely resembles ordinary tannic acid, but is coloured

green by ferric salts. When boiled with dilute acids it breaks up into sugar and *quina-red*, an amorphous brown substance, yielding protocatechuic acid and acetic acid on fusion with potassium hydroxide.

(*e*) Polyhydric Aromatic Alcohols, in which only one Hydroxyl is present in each Side Chain, and their Oxidation Products.

(1) Di- and Trihydric Aromatic Alcohols.

Xylylene Alcohols $C_6H_4(CH_2OH)_2$.—The three isomerides are obtained from the three corresponding xylylene chlorides or bromides by boiling with a soda solution. The *ortho-* (1, 2), called **phthalyl alcohol,** is obtained also from phthalic acid chloride by reduction in glacial acetic acid with a large excess of sodium amalgam (B. **12,** 646).

	M.p.		M.p.		M.p.
1, 2-Phthalyl alcohol,	62° ;	**dichloride,**	55° ;	**dibromide,**	95°.
1, 3-Xylylene alcohol,	46° ;	**dichloride,**	34° ;	**dibromide,**	77°.
1, 4-Xylylene alcohol,	112° ;	**dichloride,**	100° ;	**dibromide,**	143°.

The three chlorides are formed when the xylols are heated to 150° with PCl_5 (B. **19,** R. 24). The bromides are produced when bromine acts upon boiling xylols (B. **18,** 1281), or upon the latter in sunlight (B. **18,** 1278).

o-Xylylene oxide, *phthalane* $C_6H_4(CH_2)_2O$, b.p. 192°, a colourless oil, smelling intensely of oil of bitter almonds, is formed by heating o-xylylene bromide with caustic alkali (B. **40,** 965).

Tetrachloro-xylylene oxide $C_6Cl_4(CH_2)_2O$, m.p. 218° (A. **238,** 331).

Xylylene sulpho-hydrates $C_6H_4(CH_2.SH)_2$, 1, 2-, m.p. 46° ; 1, 3-, oil, boiling at 157° ; 1, 4-, m.p. 47°, from the xylylene bromides with alcoholic KSH. The 1, 2-xylylene sulpho-hydrate unites with aldehydes and ketones with elimination of water to *cyclic mercaptals* and *mercaptols* $C_6H_4\langle^{S}_{S}\rangle C\langle^{R}_{R'}$, from which cyclic sulphones are formed by oxidation (B. **33,** 729 ; **34,** 1772 ; **35,** 1388).

o-Xylylene sulphide $C_6H_4(CH_2)_2S$, an oil smelling like mercaptan, from o-xylylene bromide with concentrated K_2S solution besides **di-xylylene disulphide** $[C_6H_4(CH_2)_2S]_2$, m.p. 234°, which is more easily obtained from o-xylylene bromide and $C_6H_4(CH_2.SNa)_2$. Xylylene sulphide gives by oxidation **o-xylylene sulphone** $C_6H_4(CH_2)_2SO_2$, m.p. 152°, and its polymeride a **disulphone** $[C_6H_4(CH_2)_2SO_2]_2$. Dixylylene disulphide forms with Br a stable **dibromide** $(C_6H_4(CH_2)_2SBr)_2$, m.p. 111° (B. **36,** 18).

o-Xylylene-diamine $C_6H_4[1, 2](CH_2NH_2)_2$ is a liquid. It results when potassium phthalimide acts upon o-xylylene bromide (B. **21,** 578), as well as by the reduction of phthalazin. Upon heating, its chloride yields :

o-Xylylenimine, *dihydro-iso-indol* $C_6H_4(CH_2)_2NH$, boiling at 213°, also obtained by the reduction of **chloro-phthalazin** $C_6H_4\{^{CCl:N}_{CH:N}$, which has given rise to a large number of derivatives (B. **33,** 2808).

Xylylene bromide, treated with ammonia, gives **bis-xylylene-ammonium bromide** $C_6H_4(CH_2)_2C_6H_4$, which on further treatment with ammonium passes into **bis-xylylene-diamine** $[C_6H_4(CH_2)_2NH]_2$, m.p. 80°,

b.p.$_{12}$ 130°–135°. Xylylene bromide also reacts easily with primary, secondary, and tertiary amines. Primary aliphatic or aromatic amines mostly yield **n-alkyl-** or **n-aryl-xylylene-imines**; but in aromatic amines, containing substituents in ortho-position towards the NH_2 group, the closing of the ring encounters steric hindrance, and di-aryl-xylylene-diamines are formed. Secondary amines mostly form cyclic **xylylene-ammonium bromides** $C_6H_4(CH_2)_2N(RR_1)Br$, and tertiary amines form **xylylene-di-ammonium bromides**; their behaviour towards xylylene bromide may be advantageously employed in testing alkaloids (B. **40,** 852; C. 1899, I. 1246).

Like the tertiary amines, tri-ethyl phosphine combines with o-xylylene bromide to form **o-xylylene-di-triethyl-phosphonium bromide** (B. **38,** 606). m- and p-Xylylene bromide never yield cyclic derivatives with amines, but derivatives of the corresponding diamines $C_6H_4(CH_2NH_2)_2$ (B. **36,** 1672).

Pseudo-cumenyl-glycol, $CH_3[1]C_6H_3[2, 4](CH_2OH)_2$, melts at 77° (B. **19,** 867).
Mesitylene-glycol, $CH_3[1]C_6H_2[3, 5](CH_2OH)_2$, boils at 190° (20 mm.).
ω_2-Diamido-mesitylene, $CH_3.C_6H_3(CH_2NH_2)_2$, boils at 268° (B. **25,** 3017).

Mesitylene-glycerin, *mesicerine* $C_6H_3[1, 3, 5](CH_2OH)_3$ is a thick liquid (B. **16,** 2509).

o-Di-α-oxy-ethyl-benzol $C_6H_4[1, 2][CH(OH)CH_3]_2$ a yellow oil, from o-phthalic aldehyde with CH_3MgI; on boiling with dilute HCl it passes into the corresponding oxide, **1, 3-dimethyl-phthalane** $C_6H_4[CH(CH_3)]_2O$, b.p.$_{50}$ 122° (B. **41,** 986).

p-Di-α-ox-ethyl-benzol $C_6H_4[CH(OH)CH_3]_2$, liquid, from p-diacetyl-benzol (B. **27,** 2527).

α, α-Dimethyl-, di-ethyl, and **di-iso-propyl-o-xylylene alcohol** $HOCH_2.C_6H_4CR_2OH$, m.p. 64°, 82°, and 108° respectively, are formed by the action of alkyl-magnesium compounds upon phthalide. They easily pass, by splitting off water, into the corresponding oxides, called phthalanes (B. **40,** 3060).

Oxy-m-xylenols are often formed, besides the univalent phenol alcohols, by the action of formaldehyde and NaHO upon phenols (B. **40,** 2530), *e.g.* **2, 6-dimethylol-p-cresol,** *oxy-mesitylene-glycol* $HO[1]C_6H_2[4]CH_3[2, 6](CH_2OH)_2$, m.p. 130°·5, from p-cresol (B. **42,** 2539).

As might have been expected, nine classes of oxidation products are derivable from the bivalent aromatic alcohols with hydroxyls in two side chains, as in the case of the aliphatic glycols.

(2) Aldehyde Alcohols.

In this connection mention may be made of **hydro-phthalide** $C_6H_4\begin{cases}[1]CH_2\\[2]CH\end{cases}\!\!>O$, the reduction product of phthalide. It is a syrup, soluble in water. **Dimethyl-hydro-phthalide** $C_6H_4\begin{cases}[1]C(CH_3)_2\\[2]CH(OH)\end{cases}\!\!>O$, the reduction product of dimethyl-phthalide, melts at 89° (A. **248,** 61).

Phenol-aldehyde alcohols are formed synthetically from phenol-aldehydes, with formaldehyde and HCl. **o-Oxy-aldehydo-p-benzyl alcohol** $HO[1]CHO[2]C_6H_3[4]CH_2OH$, m.p. 108°, from salicyl-aldehyde (B. **34,** 2455).

(3) Aromatic Di-aldehydes.

Phthalic Acid Aldehydes $C_6H_4(CHO)_2$ corresponding to the three phthalic acids are obtained, like benzaldehyde from benzal chloride, by heating the xylylol tetrachlorides with water or potassium oxalate. They are also obtained in the form of their tetra-acetates $C_6H_4[CH(OCOCH_3)_2]_2$ by the oxidation of the three xylols, dissolved in a mixture of acetic anhydride and concentrated H_2SO_4, by means of chromic acid. The o-phthalic aldehyde, treated with ammonia, and then acidulated, gives a dark-violet coloration (A. **311**, 353).

o-Xylylol tetrachloride, or, better, o-xylylol tetrabromide and hydrazin, yield *phthalazin* $C_6H_4\begin{cases}CH:N\\CH:N\end{cases}$ (B. **28**, 1830).

o-Phthalic aldehyde, m.p. 56°; dioxime (see below).
Iso-phthalic aldehyde, ,, 89°; dioxime, m.p. 180° (A. **347**, 109).
Terephthalic aldehyde, ,, 116°; dioxime, ,, 200° (B. **16**, 2995).

The **o-, m-,** and **p-xylylol tetrachlorides** $C_6H_4(CHCl_2)_2$, corresponding to the aldehydes, are prepared by heating the three xylols with PCl_5 to 150°–190°.

The o-body melts at 89° and boils at 273°. The m-body boils at 273°, and the p-compound melts at 93°.

o-, m-, and **p-Xylylene tetrabromide** $C_6H_4(CHBr_2)_2$, m.p. 116°, 107°, and 169°, from the three xylols by the action of bromine with heat (A. **347**, 107).

Hetero-ring formations of o-phthalic aldehyde: (1) With concentrated alkalies it forms *phthalide*; (2) with acetone and benzo-phenone it condenses to *β-acetyl-* and *β-benzoyl-hydrindone*; (3) with phenylhydrazin chloride it forms *phenyl-phthalazonium chloride*; (4) with hydroxylamine it forms *phthalimidoxime*:

$$C_6H_4\begin{cases}[1]CHO\\[2]CHO\end{cases}\longrightarrow\begin{cases}\xrightarrow{KOH} C_6H_4\begin{cases}CH_2\\CO\end{cases}O & (1)\\ \xrightarrow{CH_3COCH_3} C_6H_4\begin{cases}CH_2\\CO\end{cases}CH.COCH_3 & (2)\\ \xrightarrow{C_6H_5NHNH_2} C_6H_4\begin{cases}CH=N\\CH=N\end{cases}\begin{matrix}Cl\\C_6H_5\end{matrix} & (3)\\ \xrightarrow{2NH_2OH} C_6H_4\begin{cases}C=NOH\\CO.NH\end{cases} & (4).\end{cases}$$

Mesitylene-trialdehyde $C_6H_3(CHO)_3$, m.p. 98°; its hexa-acetate is obtained from mesitylene with chromic acid and acetic anhydride (C. 1908, I. 1623).

Oxy-dialdehydes are produced together with, and from, the oxymonaldehydes by means of Reimer's reaction.

Thymo-dialdehyde $HO.C_6H(CH_3)(C_3H_7)(CHO)_2$ melts at 79° (B. **16**, 2104).

Resorcin-dialdehyde $(HO)_2.C_6H_2(CHO)_2$ melts at 127° (B. **10**, 2212).

α- and β-Orcin-dialdehydes $(HO)_2C_6H(CH_3)(CHO)_2$ melt at 118° and 168° (B. **12**, 1003).

α- and β-Oxy-iso-phthal-aldehyde $(HO)[4]C_6H_3(CHO)_2$ and $HO[2]C_6H_3(CHO)_2$ melt at 108° and 88° (B. **15**, 2022).

Oxy-uvitinic aldehyde $HO(CH_3)[1, 4]C_6H_2[2, 6](CHO)_2$, m.p. 133°, colourless needles, by oxidation of oxy-mesitylene-glycol (B. **42,** 2545).

(4) **Di- and Triketones.**—Only one acidyl group can be introduced into benzene, even by means of the aluminium chloride synthesis.

p-Diacetyl-benzol $C_6H_4[1, 4](COCH_3)_2$, m.p. 114°, is formed by the action of dilute sulphuric acid upon terephthalyl-dimalonic ester (B. **27,** 2527). **Diethyl-terephthalyl** $C_6H_4(COC_2H_5)_2$ (B. **19,** 1850). **Triacetyl-benzol** $C_6H_3[1, 3, 5](COCH_3)_3$, m.p. 163°, is formed by the benzene ring formation from formyl acetone. In the benzene homologues containing methyl groups in the meta-positions it is an easy matter, aided by Al_2Cl_6, to introduce acetyl residues between every two such methyl groups. Thus, mesitylene, durol, and iso-durol have given :

Diacetyl-mesitylene $C_6H(CH_3)_3(COCH_3)_2$, m.p. 46° and b.p. 310° ; **diacetyl-durol,** m.p. 178° and b.p. 323°–326°, and **diacetyl-iso-durol,** m.p. 121° and b.p 312°–317° (B. **28,** 3213 ; **29,** 1413).

Diaceto-resorcin $(CH_3CO)_2[1, 5]C_6H_2[2, 4](OH)_2$, m.p. 183°, from resorcin, acetyl chloride, and $ZnCl_2$ (C. 1905, I. 814).

Triaceto-phloro-glucin $(CH_3CO)_3C_6(OH)_3$, m.p. 156°, is more probably to be regarded as a derivative of triketo-hexamethylene (B. **42,** 2736).

(5) Alcohol-carboxylic Acids.

Oxy-methyl-benzoic Acids, Carbinol-benzoic Acids.—There are three possible isomerides, and all of them have been prepared. They are isomeric with almond acid and the oxy-toluic acids. o-Oxy-methyl-benzoic acid passes quite readily into the corresponding γ-lactone, **phthalide.**

Phthalide and meconin are the first lactones with which organic chemistry was enriched.

o-Oxy-methyl-benzoic acid, *benzyl-alcohol-o-carboxylic acid* $C_6H_4\begin{cases}[1]CO_2H\\[2]CH_2OH\end{cases}$, melts at 120°, loses water and becomes phthalide, from which it is obtained by dissolving in caustic alkali and then precipitating with mineral acids ; also from o-chloro-methyl-benzoic acid with moist silver oxide.

Phthalide, *o-oxy-methyl-benzoic acid lactone* $C_6H_4\begin{cases}[1]CO\\[2]CH_2\end{cases}\!\!>O$, melting at 83° and boiling at 290°, was first made from o-phthalic acid. It is formed (1) by heating o-oxy-methyl-benzoic acid or by allowing it to stand in contact with water (B. **25,** 524) ; (2) by the reduction of phthalide chloride with zinc and hydrochloric acid (B. **10,** 1445) ; (3) by the reduction of phthalic anhydride in acetic acid solution with zinc dust (B. **17,** 2178) ; (4) by the action of bromine vapour upon ortho-toluic acid at 130°–140° ; (5) from xylylene dichloride upon boiling with water and lead nitrate ; (6) by decomposing nitroso-phthalimidin obtained from phthalimide with caustic potash (A. **247,** 291) ; (7) by treating o-cyano-benzyl chloride in glacial acetic acid with hydrochloric acid at 100° (B. **25,** 3021) ; or (8) from phthalide-carboxylic acid by heating (B. **31,** 374).

It is reduced to ortho-toluic acid on boiling with hydriodic acid. Potassium permanganate oxidises it to phthalic acid. See also Phthalaldehydic acid, Phthalic acid, and ω-Cyan-o-toluic acid. Phenylhydrazin adds itself to phthalide (B. **26,** 1273 ; **33,** 766).

Numerous derivatives have been obtained from o-oxy-methyl-benzoic acid, some of which, like the acid itself, change over to heterocyclic compounds.

o-Chloro-methyl-benzoic acid $Cl.CH_2[2]C_6H_4[1]COOH$, m.p. 131°, form phthalide chloride with water, HCl being liberated; its ethyl ester, $b.p._{12}$ 141°, from phthalide chloride and alcohol (Anschütz).

It boils at 141° (12 mm.), and also, without decomposition, at 245° (760 mm.).

o-Chloro-methyl-benzoyl chloride, phthalide chloride $ClCH_2[2]C_6H_4.COCl$, boiling at 135° (12 mm.), results when PCl_5 acts upon phthalide at 55°–60°; gives anthranol with benzene and $AlCl_3$ (Anschütz).

o-Chloro-methyl-benzamide $ClCH_2[2]C_6H_4.CONH_2$ melts with decomposition at 190° (see Pseudo-phthalimidine). It is produced on conducting dry ammonia into an ethereal solution of phthalide chloride, and by the action of sulphuric acid upon its nitrile.

o-Chloro-methyl-benzanilide $Cl.CH_2[2]C_6H_4CONHC_6H_5$ melts at 115°.

o-Chloro-methyl-benzo-nitrile, o-cyano-benzyl chloride $Cl.CH_2[2]C_6H_4CN$, melting at 252°, is formed upon conducting chlorine into boiling o-tolu-nitrile (p. 286) (B. **20,** 2222). The corresponding *o-cyano-benzyl alcohol* is known only in its ethers (B. **25,** 3018).

Phthalide yields the base **phthalimidin** $C_6H_4\begin{cases}[1]CO\\[2]CH_2\end{cases}NH$, when it is heated in an atmosphere of ammonia. It can also be very readily obtained by reducing phthalimide with tin and hydrochloric acid (A. **247,** 291); from o-cyano-benzyl-amine with HCl, and from phthalide chloride by heating in a current of ammonia. It melts at 150° and boils at 337°.

Nitroso-phthalimidin $C_6H_6ON.NO$ melts at 156°. **Pseudo-phthalimidin** $C_6H_3\begin{cases}[1]C=NH\\[2]CH_2-O\end{cases}$ is an oil. In contact with water it is resolved into phthalide and ammonia. Its hydrochloride is formed when o-chloro-methyl-benzamide is heated to 130°–140°, also from phthalide chloride with alcoholic ammonia.

Phthalide anile, *phenyl-phthalimidin* $C_6H_4\begin{cases}[1]CO\\[2]CH_2\end{cases}NC_6H_5$, melting at 160°, results on heating phthalide and aniline to 200°–220°, upon reducing phthalanile with tin and hydrochloric acid, and by distilling o-chloro-methyl-benzanilide under diminished pressure (Anschütz). **o-Cyano-benzyl-amine** $NH_2.CH_2[2]C_6H_4CN$ is a colourless oil, which becomes crystalline. It is formed when o-cyano-benzyl chloride acts upon potassium phthalimide (B. **20,** 2233; **31,** 2738).

o-Diethyl-benzyl-amine-carboxylic acid $(C_2H_5)_2NCH_2C_6H_4COOH$, m.p. 105° (A. **300,** 163). **o-Cyano-benzyl-methylamine** $CNC_6H_4CH_2.NHCH_3$, m.p. 105°; **o-cyano-benzyl-aniline** $CNC_6H_4CH_2.NHC_6H_5$, m.p. 125° (*J. pr. Ch.* 2, **80,** 102).

Thio-phthalide $C_6H_4\begin{cases}[1]CO\\[2]CH_2\end{cases}S$ melts at 60° (A. **257,** 298), and—

Seleno-phthalide $C_6H_4\begin{cases}[1]CO\\[2]CH_2\end{cases}Se$ melts at 58° (B. **24,** 2596; A **247,** 299).

Thio-phthalimidin $C_6H_4\begin{cases}CH_2\\C(NH)\end{cases}S$ or **o-cyano-benzyl-mercaptan**

$C_6H_4(CN)CH_2SH$, m.p. 62°, from **o-cyano-benzyl-rhodanide** $C_6H_4(CN)CH_2SCN$, m.p. 86°, with sulphuric acid, and from o-cyano-benzyl chloride with potassium sulpho-hydrate. With excess of the latter we obtain a **dithio-phthalide** $C_6H_4\langle{}^{CH_2}_{CS}\rangle S$, m.p. 68°, which easily splits off SH_2, and passes into a stilbene derivative (B. **31**, 2646). Phthalides, substituted in the benzene nucleus, are also known; they have been mostly obtained from substituted o-phthalic acids. Mention may be made of:

p-Nitro-phthalide $NO_2C_6H_2\{{}^{[1]CO}_{[2]CH_2}\rangle O$, m.p. 135°. It is produced when chromic acid and glacial acetic acid act upon o-nitro-naphthalene (A. **202**, 219).

p-Oxy-phthalide $HO.C_6H_2\{{}^{[1]CO_2}_{[2]CH_2}\rangle O$, m.p. 222° (A. **233**, 235), is obtained from p-oxy-o-phthalic acid.

Meconin, 5, 6-*dimethoxy-phthalide* $(CH_3O)_2[5,6]C_6H_2\{{}^{[1]CO}_{[2]CH_2}\rangle O$, m.p. 102°, is the lactone of meconinic acid, which is only stable in the form of its salts. Its name is derived from the Greek word *μήκων*, signifying *poppy*.

Meconin occurs already formed in opium, in which Couerbe discovered it in 1832, and is obtained on boiling narcotin with water (Wöhler, and Liebig, 1832). It may be formed from opianic acid, the corresponding aldehyde acid, just like phthalide from phthal-aldehydic acid, by reduction with sodium amalgam and precipitation with acids. It was the first lactone known to chemistry:

$C_6H_4\{{}^{[1]CO}_{[2]CH_2}\rangle O$ Phthalide — $C_6H_4\{{}^{[1]CHO}_{[2]CO_2H}$ Phthalic aldehyde acid — $(CH_3O)_2C_6H_2\{{}^{[1]CO}_{[2]CH_2}\rangle O$ Meconin — $(CH_3O)_2C_6H_2\{{}^{CHO}_{CO_2H}$ Opianic acid.

Synthetically, meconin has been prepared from the condensation product of chloral with 2, 3-dimethoxy-benzoic ester, of **dimethoxy-trichloro-methyl-phthalide** $(CH_3O)_2C_6H_2\langle{}^{CO}_{CH(CCl_3)}\rangle O$. This yields, with alkali, an acid which, on heating, yields meconin (A. **301**, 359).

***ψ*-Meconin, 3, 4-dimethoxy-phthalide** $(CH_3O)_2[3,4]C_6H_2\{{}^{[1]CO}_{[2]CH_2}\rangle O$, m.p. 132°. It is made from hemi-pinimide, just as phthalide is formed from phthalimide (B. **20**, 884).

o-α-Oxy-ethyl-benzoic acid lactone, α-methyl-phthalide $C_6H_4\{{}^{[1]CO}_{[2]CH}\rangle O$, boils at 275°. It is formed in the reduction of aceto-phenone-o-carboxylic acid with sodium amalgam, and by the action of CH_3MgI upon o-phthalic aldehyde acid (B. **38**, 3981). Hydro-iodic acid and phosphorus reduce it to o-ethyl-benzoic acid (B. **29**, 2533).

α-Ethyl-phthalide, m.p. 12°, b.p. 291°, is obtained in a similar manner (B. **32**, 960).

Dimethyl-phthalide, o-β-oxy-iso-propyl-benzoic acid lactone $C_6H_4\{{}^{[1]CO}_{[2]C(CH_3)_2}\rangle O$, m.p. 67° and b.p. 270°, was made by the action of zinc dust and methyl iodide upon phthalic anhydride (A. **248**, 57).

Similarly, diethyl-, dipropyl-, and di-iso-propyl-phthalides have been obtained, melting at 54°, 76°, and 84° respectively (C. 1909, II. 525).

o-β-Oxy-ethyl-proto-catechuic acid lactone $C_6H_3(OH)_2\begin{cases}[1]CO\,.\,O\\[2]CH_2.CH_2\end{cases}$ is closely related to several alkaloids such as corydalin, berberin, etc.

m-Oxy-methyl-benzoic acid is only known in the form of its alcohol anhydride $O[CH_2[3]C_6H_4COOH]_2$, m.p. 180°, which is formed from **m-cyano-benzyl chloride** $Cl.CH_2[3]C_6H_4CN$, m.p. 67° and b.p. 259°, the reaction product of chlorine upon m-tolu-nitrile. **ω-Chloro-m-toluic acid** melts at 135°, and **m-benzyl-amine-carboxylic acid** $NH_2CH_2[3]C_6H_4CO_2H$ melts at 216°. *m-Cyano-benzyl-amine* $NH_2CH_2[3]C_6H_4CN$, see B. **34,** 3367.

p-Oxy-methyl-benzoic acid $HO.CH_2[4]C_6H_4CO_2H$, m.p. 181°, is obtained (1) from **p-carbinol-bromide-benzoic acid** $Br\,CH_2[4]C_6H_4.CO_2H$ (A. **162,** 342); (2) by the action of concentrated sodium hydroxide upon terephthal-aldehyde (A. **231,** 372).

p-Cyano-benzyl alcohol $HOCH_2[4]C_6H_4CN$, m.p. 133°, is prepared from **p-cyano-benzyl chloride,** m.p. 79° and b.p. 263°, by the action of potassium carbonate. **p-Chloro-methyl-benzamide** $CH_2Cl[4]C_6H_4CONH_2$, m.p. 173°. **p-Chloro-methyl-benzoic acid** $CH_2Cl[4]C_6H_4CO_2H$, m.p. 199° (B. **24,** 2416).

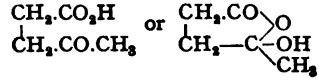
Benzyl-amine-p-carboxylic acid, yellow scales, and **diethyl-benzyl-amine-p-carboxylic acid,** m.p. 150°, see B. **23,** 1060; A. **310,** 207; p-cyano-benzyl-amine, see B. **34,** 3368.

p-Chloro-methyl-salicylic acid $ClCH_2[4]C_6H_3[1]OH[2]COOH$, m.p. 163°, from salicylic acid with formaldehyde and HCl (C. 1901, I. 1394).

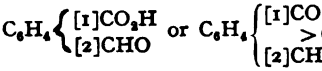
m- and **p-Oxy-iso-propyl-benzoic acids** $(CH_3)_2C(OH).C_6H_4.CO_2H$, melting at 123° and 155°, result when m-cymol (A. **275,** 159) and p-cymol, from cumic acid, are oxidised with potassium permanganate. The 3-amido-4-oxy-iso-propyl-benzoic acid, derived from the p-acid, changes under the influence of carboxylic anhydrides into *cumazonic acids* (*q.v.*).

(6) Aldehyde Acids.

o-Phthal-aldehydic acid and 5, 6-dimethoxy-o-phthal-aldehydic acid, or *opianic acid*, are the most important representatives of this class. In the phthal-aldehyde acids the aldehyde group occupies the γ-position with reference to the carboxyl group. Like the aliphatic γ-ketonic acids (the lævulinic acids, Vol. I.), the phthal-aldehyde acids form monoacetyl derivatives, whose existence and deportment argue more strongly for the γ-oxy-lactone formula (Liebermann, B. **19,** 765, 2288) than the carboxylic acid formula of such acids:



Lævulinic acid



o-Phthal-aldehydic acid.

Opianic acid forms two series of esters. Their difference is due to the fact that the one series represents carboxylic esters, while the other series consists of γ-oxy-lactone esters.

The behaviour of the oxime anhydrides of phthal-aldehydic acid and opianic acid is worthy of note. They change to the corresponding

phthalimides with an appreciable evolution of heat, when they are gently heated. The phthal-aldehydoxime-anhydridic acid first changes to o-cyano-benzoic acid, which yields phthalimide upon fusion. The determination of the heat of combustion of opian-oximic acid anhydride and hemi-pinimide has shown that in the conversion of the former into the latter the quantity of heat set free (52·6 Cal. for the gram-molecule) was tenfold greater than the molecular rearrangement-energy of allo-cinnamic into cinnamic acid, and eight times that observed in the conversion of maleïc into fumaric acid (B. **25,** 89).

o-Phthal-aldehydic acid (formulæ above), melting at 97°, is formed (1) upon heating bromo-phthalide (see below) with water; (2) by heating ω-pentachlor-o-xylol, and (3) o-cyano-benzal chloride with hydrochloric acid (B. **30,** 3197). Hydrazin converts the acid into *phthalazone* (*q.v.*) $C_6H_4\begin{cases}[1]CO—NH\\[2]CH=N\end{cases}$, melting at 183°; phenyl-hydrazin changes it to *phenyl-phthalazone*, melting at 105° (B. **26,** 531), and hydroxylamine, in aqueous solution, into **benzaldoxime-o-carboxylic acid,** melting at 120°; while in alcoholic solution the product is **benzaldoxime-o-carbonic anhydride,** benzo-ortho-oxazinone, melting at 145°. The latter at 145° rearranges itself with evolution of much heat into o-cyano-benzoic acid, which at more elevated temperatures becomes *phthalimide* (B. **26,** 3264):

$$C_6H_4\begin{cases}[1]COOH\\[2]CH=NOH\end{cases}\rightarrow C_6H_4\begin{cases}[1]COO\\[2]CHN\end{cases}\rightarrow C_6H_4\begin{cases}[1]COOH\\[2]C\equiv N\end{cases}\rightarrow C_6H_4\begin{cases}[1]CO\\[2]CO\end{cases}NH.$$

Benzaldoxime-o-carboxylic acid — Benzaldoxime-o-carboxylic acid anhydride — o-Cyano-benzoic acid — o-Phthalimide.

With benzoyl-hydrazin and β-phenyl-hydroxylamine also phthal-aldehydic acid and opianic acid first form aldehyde derivatives (B. **34,** 1017).

Methoxy-phthalide, *phthal-aldehydic methyl ether*, melting at 44°; **ethoxy-phthalide,** melting at 66°; and **amido-phthalide,** *amide of phthal-aldehydic acid*, are produced by the action of methyl and ethyl alcohol, and of ammonia upon **bromo-phthalide,** or the *bromide of phthal-aldehydic acid*, melting at 85°, produced when bromine vapour acts upon phthalide at 140°. **Aceto-phthal-aldehydic acid,** *acetoxy-phthalide*, is formed by the interaction of acetic anhydride and phthal-aldehydic acid.

Diphthalide ether $C_6H_4\begin{cases}[1]CO\\[2]CH\end{cases}>O\;O<\begin{cases}CO[1]\\CH[2]\end{cases}C_6H_4$, melting at 221°, is formed from o-phthal-aldehydic acid and bromo-phthalide. In accordance with the double formulation of phthal-aldehydic acid (see above) two views may be held in regard to its various derivatives:

$C_6H_4\begin{cases}[1]COOCH_3\\[2]CHO\end{cases}$ $C_6H_4\begin{cases}[1]CONH_2\\[2]CHO\end{cases}$ $C_6H_4\begin{cases}[1]COBr\\[2]CHO\end{cases}$ $C_6H_4\begin{cases}[1]COOCOCH_3\\[2]CHO\end{cases}$

$C_6H_4\begin{cases}[1]CO>O\\[2]CH—OCH_3\end{cases}$ $C_6H_4\begin{cases}[1]CO>O\\[2]CH—NH_2\end{cases}$ $C_6H_4\begin{cases}[1]CO>O\\[2]CHBr\end{cases}$ $C_6H_4\begin{cases}[1]CO>O\\[2]CH—OCOCH_3\end{cases}$

Methoxy-phthalide — Amido-phthalide — Bromo-phthalide — Acetoxy-phthalide.

The theory that acetoxy-phthalide and the diphthalide ethers are anhydrides of carboxylic acids is very improbable. Phthal-aldehydic acid and opianic acid react especially readily, even in the cold, with

amines. Water is eliminated. The resulting bodies dissolve in part very easily in soda, and in part with difficulty, hence are in part derived from the amido-phthalide and partly from the imido-aldehydic acid formula (B. **29,** 174, 2030).

$$C_6H_4\begin{cases}[1]CO>O\\[2]CH—NHR\end{cases} \quad \text{and} \quad C_6H_4\begin{cases}[1]COOH\\[2]CH=NR.\end{cases}$$

Phthal-aldehyde Chlorides.—**Pentachloride of o-phthal-aldehydic acid,** *n-pentachlor-o-xylol* $CHCl_2[2]C_6H\,CCl_3$, melting at 53°, results when PCl_5 acts upon o-xylol at 140°. **o-Cyano-benzal chloride,** nitrile of o-phthal-aldehyde chloride acid, $CHCl_2[2]C_6H_4CN$, boiling at 260°, is formed by the action of chlorine upon boiling o-cyano-toluol (B. **20,** 3197).

Nor-opianic acid, 5, 6-*dioxy-phthal-aldehydic acid* $(HO)_2C_6H_4(CHO)COOH$, melting at 171°, is obtained from opianic acid, together with iso-vanillin and carbon dioxide, upon heating with hydriodic acid. It is coloured bluish-green by ferric chloride.

Opianic acid, 5, 6-*dimethoxy-phthal-aldehydic acid* $(CH_3O)_2[5,6]C_6H_2[2]CHO.CO_2H$, melting at 150°, is produced on oxidising narcotin with dilute sulphuric acid and MnO_2 (1842, Wöhler and Liebig, A. **44,** 126). Meconin is formed in its reduction. When it is evaporated with caustic potash it changes in part to meconin and partly to hemi-pinic acid, just as benzaldehyde yields benzyl alcohol and benzoic acid. It is oxidised to hemi-pinic acid. Upon heating with hydrochloric acid there results at first: **5-Methoxy-6-oxy-phthal-aldehydic acid,** *methyl-nor-opianic acid* $(CH_3O)[5](HO)[6]C_6H_2(CHO)CO_2H$, melting at 154° (B. **30,** 691), while under more intense heat iso-vanillin and CO_2 are the products. Concentrated sulphuric acid converts opianic acid into *rufiopin* (*q.v.*), a tetra-oxy-anthraquinone derivative.

Opianic acid behaves toward hydrazin, phenyl-hydrazin, and hydroxylamine just like phthal-aldehydic acid. **Dimethoxy-phthal-azone,** *opiazone,* melts at 162°, when it is anhydrous (B. **27,** 1418). **Phenyl-opiazone** melts at 175° (B. **19,** 2518). **Opianoximic acid,** melting at 82°, becomes, on boiling its aqueous solution, the **anhydride of opianoximic acid,** melting at 114°. When this is heated alone, or when its alcoholic solution is boiled, hemi-pinimide results as a consequence of rearrangement (B. **24,** 3264).

Esters.—Opianic acid forms two series of alkyl esters, corresponding to the carboxylic and to the γ-oxy-lactone formulas of the acid. The one series, the true carboxylic esters, are stable in the presence of water. They are formed by the action of alkyl iodides upon the silver salt or of alcohols upon the chloride of opianic acid, and by esterifying opianic acid with diazo-methane.

They manifest the typical aldehyde reactions (B. **29,** R. 507). The second series, the γ-oxy-lactones or ψ-esters, are formed on boiling opianic acid with alcohols: **Methyl-opianic ester** $(CH_3O)_2C_6H_2(CHO)CO_2CH_3$, melts at 82° and boils at 233° (51 mm.). The ethyl ester melts at 64°. **ψ-Methyl-opianic ester** $(CH_3O)_2C_6H_2\begin{cases}CH>O\\CO—OCH_3,\end{cases}$ m.p. 103°, and b.p. 238° (52 mm.). The ψ-ethyl ester melts at 92° (B. **25,** R. 907; **26,** R. 700).

Acetyl-opianic acid melts at 120° (B. **19,** 2288). **[3]-Nitro-opianic acid,** m.p. 166°, has an abnormally low affinity constant in aqueous

solution, and therefore probably corresponds to the oxy-lactone from (B. **36,** 1541); **methyl ester,** m.p. 78°; **ψ-methyl ester,** m.p. 182° (C. 1904, I. 163).

It yields by reduction **dimethoxy-anthranilo-carboxylic acid, azo-opianic acid** $(CH_3O)_2C_6H(COOH)\begin{cases}N-\\CH\end{cases}>O$, which upon treatment with acetone and sodium hydroxide condenses to **acetonil-nitro-meconin** $(CH_3O)_2C_6H(NO_2)\begin{cases}CH(CH_2COCH_3)\\CO\end{cases}>O$, m.p. 175°, and opian-indigo (B. **36,** 2208).

Pseudo-opianic acid $(CH_3O)_2[3,4]C_6H_2[2](CHO)CO_2H$, m.p. 121°, is formed from berberal, an oxidation product of the alkaloid *berberin* (*q.v.*), when it is boiled with dilute sulphuric acid. Amido-ethyl-piperonyl-carboxylic anhydride (B. **24,** R. 158) is formed simultaneously. The **oxime,** melting at 124°, is rearranged upon heating into hemipinimide (B. **24,** 3266).

m-Aldehydo-benzoic acid, *iso-phthal-aldehydic acid* $CHO[3]C_6H_4CO_2H$, melts at 165°. **m-Cyano-benzaldehyde** melts at 80°. **m-Cyano-benzal chloride** boils at 274° (B. **24,** 2416). **p-Aldehydo-benzoic acid, terephthal-aldehydic acid** $CHO[4]C_6H_4CO_2H$ melts at 285°. **p-Cyano-benzaldehyde** melts at 97°. **p-Cyano-benzal chloride** boils at 275° (B. **24,** 2422).

Mono- and dioxy-aldehydo-acids have been obtained from mono- and dioxy-carboxylic acids by means of chloroform and caustic alkali (B. **12,** 1334; **16,** 2182). Similarly, anthranilic acid, with chloroform and alkali, yields an **aldehydo-o-amido-benzoic acid** (C. 1900, I. 812).

(7) Ketone-carboxylic Acids.

o-Aceto-phenone-carboxylic acid is the most important of the aromatic monocarboxylic acids with keto- and carboxyl-groups in different side chains. In it the γ-position imparts to the keto- and carboxyl-groups reactions similar to those manifested by o-phthal-aldehydic acid. Hence, in addition to the carboxylic acid formula we must also consider the γ-oxy-lactone formula for o-aceto-phenone-carboxylic acid. Its acetyl compound must be viewed as acetyl-γ-oxy-lactone:

$$C_6H_4\begin{cases}[1]COOH\\[2]COCH_3\end{cases} \text{ or } C_6H_4\begin{cases}[1]CO>O\\[2]C(OH)CH_3\end{cases} \quad C_6H_4\begin{cases}[2]CO>O\\[2]C(OCOCH_3)CH_3\end{cases}.$$

o-Aceto-phenone-carboxylic acid, *o-aceto-benzoic acid,* m.p. 115°, is isomeric with benzoyl-acetic acid (*q.v.*) and tolyl-glyoxylic acid (*q.v.*). It has a sweet taste, and is formed on boiling benzoyl-aceto-o-carboxylic acid with water (B. **26,** 705; **29,** 2533). The *acetyl compound* melts at 70° (B. **14,** 921). Hydrazin converts it into **methyl-phthalazone,** m.p. 220° and b.p. 247° (B. **26,** 705). With phenyl-hydrazin it yields **methyl-n-phenyl-phthalazone,** melting at 102° (B. **18,** 803). Its ethyl ester and hydroxylamine form an *oxime anhydride,* m.p. 158° (B. **16,** 1995).

Various homologous o-acidyl-benzoic acids have been obtained by digesting their anhydrides, the alkylidene-phthalides, with potassium hydroxide. These anhydrides are produced in the condensation of phthalic anhydride and fatty acids, when water and carbon dioxide

are eliminated. **o-Butyro-phenone-carboxylic acid** and **o-iso-valero-phenone-carboxylic acid** melt at 89° and 88° (B. **29,** 1437; **32,** 959).

p-Aceto-phenone-carboxylic acid melts at 200°. It results from the oxidation of p-β-oxy-iso-propyl-benzoic acid (A. **219,** 260). **p-Cyan-aceto-phenone,** m.p. 60°, is made from p-amido-aceto-phenone (B. **20,** 2955).

Methyl-benzyl-ketone-o-carboxylic acid $COOH[2]C_6H_4CH_2COCH_3$, m.p. 119°, is formed from methyl-iso-cumarin (*q.v.*) by boiling with alkalies (B. **32,** 965).

Benzyl-acetone-o-carboxylic acid $COOH[2]C_6H_4[1]CH_2.CH_2.COCH_3$, m.p. 114°, see B. **40,** 189.

Polycarboxylic Acids.—Three varieties are to be distinguished in each group of these acids: those in which all the carboxyl groups are directly joined to the benzene nucleus; those in which these groups are in part joined to the nucleus and are in part present in the side chains; and, lastly, those in which all of the carboxyl groups are contained in the side chains, *e.g.*:

$C_6H_4\{^{COOH}_{COOH}$	$C_6H_4\{^{CH_2CO_2H}_{CO_2H}$	$C_6H_4\{^{CH_2CO_2H}_{CH_2CO_2H}$
Phthalic acids	Homo-phthalic acids	Phenylene-diacetic acids.

(8) Dicarboxylic Acids

(*a*) **Phthalic acids** are the final oxidation products of all benzene derivatives in which two hydrogen atoms of the benzene nucleus have been replaced by side chains. Hence they are of importance in determining the position of these two side groups in the benzene nucleus. Their hydrogen addition products, the *hydro-phthalic acids,* are also very important compounds from a theoretical standpoint. Again, o-phthalic acid is distinguished from the m- and p-bodies by its ability to form an anhydride and other cyclic derivatives. In addition to the dicarboxyl formula, the γ-dioxy-lactone formula has been taken into consideration for this acid. It is applied technically in the manufacture of phthaleïn-dye substances, which are of great value. The phthalic acids bear the same relation to the phthalyl alcohols, the phthal-aldehydes, oxy-methyl-benzoic acids, and phthal-aldehydic acids, that oxalic acid bears to ethylene-glycol, glyoxal, glycollic acid, and glyoxalic acid:

CH_2OH CH_2OH	CHO CHO	$COOH$ CH_2OH	$COOH$ CHO	$COOH$ $COOH$
Glycol	Glyoxal	Glycollic acid	Glyoxalic acid	Oxalic acid.
$C_6H_4\{^{CH_2OH}_{CH_2OH}$	$C_6H_4\{^{CHO}_{CHO}$	$C_6H_4\{^{COOH}_{CH_2OH}$	$C_6H_4\{^{COOH}_{CHO}$	$C_6H_4\{^{COOH}_{COOH}$
Phthalyl-alcohols	Phthal-aldehydes	Oxy-methyl-benzoic acids	Phthal-aldehyde acids.	Phthalic acids.

Phthalic acid, *benzene-o-dicarboxylic acid* $C_6H_4\{^{[1]COOH}_{[2]COOH}$, $C_6H_4\{^{C(OH)_2}_{CO}\!\!>\!O$ (A. **269,** 155), melts, when rapidly heated, at 213°, decomposing at the same time into the anhydride and water. It is obtained by oxidising naphthalene and tetrachloro-naphthalene with nitric-acid permanganates (B. **36,** 1805), or best with concentrated

H_2SO_4 and mercuric sulphate (German patent 91,202). It is manufactured on a large scale. It is formed from the naphthalene together with benzoic acid on heating with NaHO and copper oxide to 240°–260° (C. 1903, I. 857).

It also results on oxidising o-xylol and o-toluic acid with potassium permanganate, alizarin and purpurin with nitric acid, or with manganese dioxide and sulphuric acid ; and, in slight amount, in the oxidation of benzene and benzoic acid. It cannot be prepared by using chromic acid as an oxidising agent, since the latter burns it at once to carbon dioxide. It can be synthetically obtained from o-nitro-benzoic acid by converting the latter into o-cyano-benzoic acid, and then boiling this with alkalies.

History.—Laurent first obtained the acid, in 1836, by oxidising naphthalene tetrachloride. He considered it a naphthalene derivative, and named it naphthalinic acid (A. **19,** 38). After Marignac had deduced the correct formula, $C_8H_6O_4$ (A. **38,** 13), and demonstrated that the acid was not a derivative of naphthalene, Laurent gave it the name phthalic acid (A. **41,** 107).

When heated with excess of calcium hydroxide it yields benzene and $2CO_2$. Only $1CO_2$ is split off, and calcium benzoate produced, if its lime salt be heated to 330°–350° with one molecule of $Ca(OH)_2$.

Sodium amalgam converts phthalic acid into di-, tetra-, and hexahydrophthalic acids.

Esters.—As the investigation of phthalyl chloride seemed to assign a lactone formula to this body, in which the two chlorine atoms were attached to the same carbon atom, search was made for two series of esters. However, the action of alkyl iodides upon the silver salt, and that of alcohols upon the chloride, produced the same esters (A. **238,** 318). The *methyl ester* boils at 280° and the *ethyl ester* at 288° (B. **16,** 860). These esters condense with acetic ester, acetone, and similar bodies in the presence of sodium ethylate, forming *diketo-hydrindene* derivatives. The *phenyl ester* melts at 70° (B. **7,** 705 ; **28,** 108). The *ethyl ester acid* is a heavy oil.

Chlorides.—The chloride of the ethyl-ester acid is a decomposable oil, produced when PCl_3 acts upon the ethyl-ester acid (B. **20,** 1011).

Phthalyl chloride $C_6H_4\begin{cases}[1]COCl\\[2]COCl\end{cases}$ or $C_6H_4\begin{cases}[1]CO\\[2]CCl_2\end{cases}O$, solidifies at 0° and boils at 275°. It results upon heating the anhydride for several hours with an equi-molecular quantity of PCl_5 at 200° (A. **238,** 329). The conversion of phthalyl chloride with glacial acetic acid and sodium amalgam into o-phthalyl alcohol is an argument favouring the sym. formula. The unsym. formula is evident from conversion of the chloride by zinc and acetic acid into phthalide, diphthalyl $C_6H_4\begin{cases}CO>O\\C=\!=\!=C\end{cases}\begin{matrix}O<CO\\\end{matrix}\}C_6H_4$ and hydro-diphthalyl, and with benzene and aluminium chloride into phthalo-phenone or diphenyl-phthalide.

With lead thio-phenate, phthalyl chloride is converted into **bi-thiophenyl-phthalide** $C_6H_4\begin{cases}C(SC_6H_5)_2\\CO\text{———}\end{cases}>O$, m.p. 85°. This is oxidised by permanganate to **diphenyl-sulphone-phthalide,** m.p. 194°, which is also formed direct from phthalyl chloride with sodium benzol sulphonate (*J. pr. Ch.* 2, **66,** 345).

Phthalylene Tetrachlorides.—PCl_5 converts phthalyl chloride into two **phthalylene tetrachlorides,** melting at 88° and 47°. These cannot be changed into one another. Their crystals have been measured. Both yield phthalic acid, and have been assigned the formulas $C_6H_4\begin{cases}CCl_2\\COCl\end{cases}$ and $C_6H_4\begin{cases}CCl_2\\CCl_2\end{cases}O$. The formation of the two chlorides is only comprehensible from the unsymmetrical phthalyl-chloride formula (B. **19,** 1188). The chloride, melting at 88°, is also obtained in the action of PCl_5 upon phthalide chloride. This reaction argues for the unsymmetrical formula, just as well as the conversion into diphenyl-anthrone (see this) by condensation with benzene by means of Al_2Cl_6 or concentrated sulphuric acid (B. **28,** R. 772).

Phthalic anhydride $C_6H_4\begin{cases}[1]CO\\[2]CO\end{cases}O$, melting at 128° and boiling at 284°, sublimes readily in long needles. It results upon fusing phthalic acid or digesting it with acetyl chloride (B. **10,** 326). Phthalic anhydride yields condensation products as readily as benzaldehyde.

Thus phthalyl-acetic acid is formed on boiling the anhydride with acetic anhydride. It reacts in like manner with malonic ester and aceto-acetic ester. At more elevated temperatures it combines with homologous fatty acids, with the elimination of CO_2 and the formation of alkylidene-phthalides. It condenses with phthalide to diphthalyl (see this). With the phenols it yields the important phthaleïn dyes (see these), a group of triphenyl-methane dyes, comprising certain beautifully fluorescent compounds. **Thio-phthalic anhydride** $C_6H_4(CO)_2S$ melts at 114° and boils at 284° (B. **17,** 1176).

Phthalo-mono-super acid (?) $C_6H_4(COOH)COOOH$, m.p. 110°, with conversion into phthalic acid, and **peroxide-phthalic acid** $(COOH.C_6H_4.CO)_2O_2$, m.p. 156° with decomposition, are formed by shaking up phthalyl anhydride with alkaline H_2O_2 solution; the former dissolves in water easily, the latter with difficulty.

Peroxide-phthalic acid diethyl ester $O_2(CO.C_6H_4COOC_2H_5)_2$, m.p. 59°, from phthal-ethyl ester chloride with alkaline H_2O_2.

Phthalyl peroxide $C_6H_4(CO_2)_2$ melts at 133°, giving gas evolution. When heated rapidly to 136° it explodes. It is formed when phthalyl chloride is acted upon with a sodium peroxide solution (B. **27,** 1511).

Phthalamic acid $C_6H_4\begin{cases}[1]COOH\\[2]CONH_2\end{cases}$ or $C_6H_4\begin{cases}[1]C(NH_2)(OH)\\[2]CO\text{———}\end{cases}O$, melting at 148°, is formed from the anhydride and ammonia, or when baryta water acts upon phthalimide (B. **19,** 1402). **Anilic acid** melts at 192°. **Phthalic diamide** $C_6H_4\begin{cases}[1]CONH_2\\[2]CONH_2\end{cases}$ or $C_6H_4\begin{cases}[1]C(NH_2)_2\\[2]CO\text{———}\end{cases}O$ melts at 140°–160°, changing at the same time to phthalimide. It is produced when ammonia acts upon the ester (B. **19,** 1399; **21,** R. 612; **24,** R. 320; **25,** R. 911).

Phthalimide $C_6H_4\begin{cases}[1]CO\\[2]CO\end{cases}NH$ or $C_6H_4\begin{cases}[1]C(=NH)\\[2]CO\text{———}\end{cases}O$, melting at 238°, is obtained:

By heating phthalic anhydride or chloride in ammonia gas;

By heating phthalic acid with ammonium sulpho-cyanide (B. **19,** 2283); from phthalamide, and

By the molecular rearrangement of the isomeric o-cyano-benzoic acid.

It forms **potassium phthalimide** $C_6H_4(CO)_2NK$ by the action of alcoholic potash.

Salts of the heavy metals can be obtained from it by double decomposition. Potassium phthalimide is readily rearranged, or transposed, with organic halogen derivatives; consequently it is frequently employed in the preparation of numerous amines. While by this means alkylogens yield *symmetrical alkylimides* of the formula $C_6H_4(CO)NR$ —*e.g.* **sym. methyl-** and **benzyl-phthalimide,** melting at 132° and 115°,—unsymmetrical alkylimides of the formula $C_6H_4\begin{cases}C:(NR)\\CO\text{——}\end{cases}O$ are obtained from the interaction of phthal-alkylamic acids and acetyl chloride: **unsym. methyl-** and **benzyl-phthalimide** melt at 78° and 81° (B. **27,** R. 737).

On brominating sym. methyl-phthalimide we obtain **bromo-methyl-phthalimide** $C_6H_4(CO)_2NCH_2Br$, m.p. 150°; on heating with water this becomes **oxy-methyl-phthalimide** $C_6H_4(CO)_2N.CH_2OH$, m.p. 142°, also obtained from phthalimide with formaldehyde, at 100°, and easily dissolved again into these constituents; by condensation with benzols by means of concentrated sulphuric acid, oxy-methyl-phthalimide is converted into benzyl-phthalimides (C. 1902, II. 1164). From ethyl-phthalimide with alkyl-magnesium haloids we get products of the formula $C_6H_4\begin{cases}CO\text{——}\\C(OH)Alk\end{cases}NC_2H_5$ (B. **37,** 385).

On reduction, phthalimide becomes phthalimidin; with bromine and alkaline hydrate it becomes anthranilic acid. The **bromyl-phthalimide** $C_6H_4(CO)_2NBr$ occurring as an intermediate product in the latter reaction, and melting at 206° or 207°, is also obtained from sodium phthalimide with one molecule bromine in aqueous solution at 0°; **chloryl-phthalimide** $C_6H_4(CO)_2NCl$, m.p. 183°–185°, is obtained by the action of chlorine upon phthalimide shaken up with water (C. 1903, I. 744). With sodium alcoholates these compounds give, in the first instance, carbox-alkyl-anthranilic acid ester (B. **33,** 21).

From phthalic acid and aniline we obtain **sym. phthalanile** $C_6H_4(CO)_2NC_6H_5$, m.p. 208°. **Unsym. phthalanile** $C_6H_4\begin{cases}C(NC_6H_5)\\CO\text{——}\end{cases}O$, m.p. 116°, is obtained from phthalanilic acid with acetyl chloride (B. **32,** 1991; **36,** 996; C. 1903, II. 432).

Phthalyl-phenyl-hydrazide $C_6H_5(CO)_2(NHNHC_6H_5)_2$ melts at 161°. **Phthalyl-hydrazin** $C_6H_4(CO)_2(NH)_2$, from phthalic anhydride and hydrazin hydrate, sublimes at 200°. Phthalimide and hydrazin yield an isomeric phthal-hydrazin (B. **28,** R. 429; **29,** R. 987).

α-Phthalyl-phenyl-hydrazin $C_6H_4(CO)_2N.NHC_6H_5$ melts at 178°.

β-Phthalyl-phenyl-hydrazin $C_6H_4\begin{cases}CONH\\CONC_6H_5\end{cases}$ melts at 210° (B. **19,** R. 303; **20,** R. 255).

Phthalyl-hydroxylaminic acid $C_6H_4(COOH)C(OH)NHOH$, m.p. 220° with decomposition, from cold phthalic anhydride and hydroxylamine. On heating the solution it becomes **phthalyl-hydroxylamine** $C_6H_4(CO_2)NOH$, m.p. 230°; both bodies are transformed into anthranilic acid by treatment with alkali (C. 1902, I. 1083; II. 1286, 1439).

Phthalyl-glycocoll $C_6H_4(CO)_2NCH_2COOH$, m.p. 192°, formed by introducing glycocoll into molten phthalic anhydride; sodium ethylate transposes the ester into the iosmeric oxy-iso-carbo-styrile-carboxylic

ester (*q.v.*) (B. **33,** 981 ; **40,** 4409) ; the chloride, m.p. 85°, decomposes on distillation, at ordinary pressure, into CO and chloro-methyl-phthalimide $C_6H_4(CO)_2N.CH_2Cl$. **Phthalyl-alanin** $C_6H_4(CO)_2N.CH(CH_3)CO_2H$, m.p. 162° ; chloride, m.p. 73°. **β-Phthalimido-propionic acid** $C_6H_4(CO)_2N.CH_2.CH_2CO_2H$, m.p. 151° ; chloride, m.p. 108° (B. **38,** 633 ; **41,** 242).

Nitriles of Phthalic Acid.—**o-Cyano-benzoic acid** is produced when anthranilic acid is treated with nitrous acid and cuprous cyanide. It rearranges itself, upon the application of heat, into phthalimide (B. **18,** 1496 ; **19,** 2283 ; **25,** R. 910). **o-Cyano-benzoic acid ester** melts at 70° (B. **19,** 1491). **o-Cyano-benzo-trichloride** $CN[2]C_6H_4CCl_3$, m.p. 94° and b.p. 280°, is obtained from o-tolu-nitrile (B. **20,** 3199). **o-Cyano-benzamide, o-phthalo-nitrilamide**, is formed, besides other products, on brief heating of phthalimide with acetic anhydride, and in the transformation of o-cyano-benzol chloride with hydroxylamine. On heating above the m.p. (173°), it passes into the isomeric imido-phthalimide ; and, on boiling with excess of acetic anhydride, into o-phthalo-nitrile (B. **40,** 2709).

o-Phthalo-nitrile $C_6H_4[1,2](CN)_2$, m.p. 141°, is also obtained from o-amido-benzo-nitrile through the diazo-compound (B. **29,** 630).

Substituted o-Phthalic Acids are obtained, partly by direct substitution of the phthalic acid, and partly by the oxidation of substituted naphthalins and toluic acids.

All the mono- and dichloro-phthalic acids are known :

4-Chloro-phthalic anhydride	m.p. 98°	b.p. 297°		
3-Chloro-phthalic anhydride	„ 122°	„ 313°		
4, 5-Dichloro-phthalic anhydride	„ 186°	„ 313°	}	
3, 4-Dichloro-phthalic anhydride	„ 121°	„ 329°	}	(B. **42,** 3532)
3, 6-Dichloro-phthalic anhydride	„ 191°	„ 339°	}	
3, 5-Dichloro-phthalic anhydride	„ 89°			(C. 1903, I. 140)
3, 4, 6-Trichloro-phthalic anhydride	„ 148°			(B. **34,** 2107)
Tetrachloro-phthalic anhydride	„ 250°			(A. **149,** 18).

The mono-, tri-, and tetrachloro-phthalic acids have been obtained by oxidation of the corresponding chlorinated o-toluic acids or naphthalins. 4, 5-, 3, 4-, and 3, 6-dichloro-phthalic acids are formed together, on conducting chlorine into a solution of phthalic anhydride in fuming sulphuric acid ; and the 3, 5-acid in small quantity by the action of PCl_5 upon dimethyl-dihydro-resorcin (*q.v.*).

4, 5-Dibromo-phthalic acid, m.p. 135°, and *anhydride*, m.p. 214°, from phthalic anhydride with bromine in concentrated sulphuric acid, or by oxidation of dibromo-naphthalin with nitric acid. On boiling with KHO it gives dioxy-phthalic acid (B. **34,** 2741 ; C. 1907, I. 1119).

3- and **4-Iodo-o-phthalic acids** melt at 206° and at 182° (B. **29,** 1575. R. 792). **Tetra-iodo-o-phthalic acid** melts at 324°–327° (B. **29,** 1634), **3-** and **4-Nitro-o-phthalic acids,** melting at 219° and 161° respectively, are formed together on nitrifying phthalic acid ; the anhydrides melt at 164° and 114°, the imides at 216° and 202°. **3-Nitro-phthalyl chloride,** m.p. 77° (B. **34,** 3735, 4351 ; C. 1902, II. 359 ; 1903, II. 430). Concerning the formation of **3-nitro-phthalic ester acids,** α-, m.p. 144°, and β-, m.p. 157°, and their relation to V. Meyer's esterification rule,

see B. **35,** 3857. On reduction of nitro-phthalic acids, **3-** and **4-amido-phthalic acids** are formed (B. **36,** 2494).

Sulpho-o-phthalic acid is obtained by heating naphthols, naphthylamines, and naphthalene-sulphonic acids with concentrated sulphonic acid and mercury to 220°–300° (B. **29,** 2806).

Oxy-o-phthalic acids.—They are recognised by the melting-points of their anhydrides, into which they change upon the application of heat.

3-Oxy-o-phthalic acid anhydride melts at 147° (B. **16,** 1965). **Dinitro-3-oxy-o-phthalic acid** is *juglonic acid*, which can also be obtained by the action of nitric acid upon juglone, a naphthalene derivative (B. **19,** 168; C. 1907, I. 1120). **4-Oxy-o-phthalic acid anhydride** melts at 165° (A. **238,** 232). **p-Dioxy-o-phthalo-nitrile,** *o-dicyano-hydroquinone* $(HO)_2[3,6]C_6H_2[1,2](CN)_2+2H_2O$, is formed from quinone with nascent prussic acid; on heating with concentrated sulphuric acid it becomes **dioxy-phthalimide** $C_6H_2(OH)_2(CO)_2NH$, which, on boiling with HCl, splits off CO_2 and becomes p-dioxy-benzoic acid (B. **33,** 675; A. **349,** 45).

Nor-hemi-pinic acid, 3, 4-dioxy-phthalic acid anhydride, melting at 238°, is produced when **3, 4-dichloro-methoxy-phthalic acid anhydride** $(ClCH_2O)_2C_6H_2(CO)_2O$, m.p. 156°—the reaction product of PCl_5 and hemi-pinic acid at 180°—is digested with water. **Hemi-pinic anhydride, 3, 4-dimethoxy-phthalic anhydride,** melts at 167°. The acid is formed, together with opianic acid and meconin, in the oxidation of *narcotin*; also with meconin on fusing opianic acid with caustic potash:

$$(CH_3O)_2C_6H_2\begin{cases}COOH\\COOH\end{cases} \longleftarrow (CH_3O)_2C_6H_2\begin{cases}COOH\\CHO\end{cases} \longrightarrow (CH_3O)_2C_6H_2\begin{cases}CO\\CH_2\end{cases}\!\!>O$$

Hemi-pinic acid — Opianic acid — Meconin.

Consult B. **29,** R. 96, for the hemi-pinamido-acids, the hemi-pinic esters, and the hemi-pinimides.

6-Amido-hemi-pinic acid is produced on boiling its anhydride with baryta water. The anhydride is **azo-opianic acid** or **2, 3-dimethoxy-5, 6-anthranile-carboxylic acid.**

Nor-meta-hemi-pinic anhydride melts at 247°. **Meta-hemi-pinic anhydride** melts at 175°. **Meta-hemi-pinic acid** or **4, 5-dimethoxy-o-phthalic acid** was obtained in the decomposition of *papaverin* (B. **24,** R. 902). *Methylene-meta-hemi-pinic ether acid* $(CH_2O_2)C_6H_2(COOH)_2$ is **hydrastic acid,** formed in the oxidation of *hydrastinine*. The oxidation of *cotarnine* yields **cotarnic acid** or *methylene-methyl ether*—3, 4, 5-*trioxy-o-phthalic acid* $(CH_2O_2)(CH_3O)C_6H(COOH)_2$.

Iso-phthalic acid, benzene-m-dicarboxylic acid $C_6H_4\begin{cases}[1]CO_2H\\[3]CO_2H\end{cases}$ melts above 300° and sublimes. It is formed by oxidising m-xylol and m-toluic acid with a chromic acid mixture or permanganate (B. **36,** 1798); by the further oxidation of m-phthalyl alcohol ethyl ether, obtained from m-xylylene bromide and alcoholic potash (B. **21,** 47), and from m-dicyano-benzol and m-cyano-benzoic acid. The last two methods permit of nuclear syntheses from the corresponding amido-compounds, m-phenylene-diamine and m-amido-benzoic acid.

The acid is also formed when potassium m-sulpho-benzoate,

m-bromo-benzoate, and benzoate are fused with potassium formate (terephthalic acid is also formed in the last two cases); by the action of the ester of chloro-carbonic acid and sodium amalgam upon m-dibromo-benzene; also by heating hydro-pyro-mellitic and hydro-prehnitic acids.

Iso-phthalic acid is soluble in 460 parts boiling and 7800 parts cold water. It does not yield an anhydride. Reduction changes it to tetrahydro-iso-phthalic acid. The *barium salt* $C_6H_4(CO_2)_2Ba+6H_2O$ (A. **260**, 30) is very soluble in water (distinction between phthalic and terephthalic acids).

The *dimethyl ester* melts at 64°.

The *dichloride* melts at 41° and boils at 276°. The *dihydrazide* melts at 220°. Nitrous acid converts it into **iso-phthalazide** $C_6H_4(CON_3)_2$, melting at 56°. Boiling alcohol converts it into m-phenylene-urethane $C_6H_4(NHCO_2C_2H_5)_2$ (B. **29**, R. 987).

m-Cyano-benzoic acid melts at 217° (B. **20**, 524).

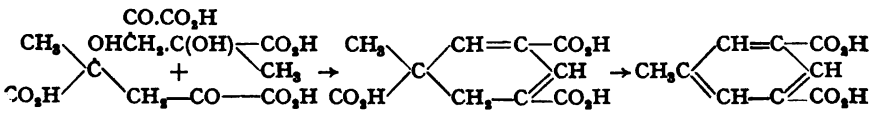
m-Dicyano-benzol melts at 158° (B. **17**, 1430).

Substituted Iso-phthalic Acids.—The **5-chloro-**, **5-iodo-**, and **5-amido-phthalic acids** can be prepared from 5-nitro-iso-phthalic acid. The nitration and sulphonation of iso-phthalic acid produce **5-nitro-iso-phthalic acid** and **5-sulpho-iso-phthalic acid** (see Benzoic acid). The **4-bromo-**, **4-iodo-**, **4-amido-**, and **4-sulpho-iso-phthalic acids** are obtained by the oxidation of the corresponding toluic acids (B. **24**, 3778; **28**, 84; **25**, 2795; **14**, 2278). **2-Nitro-** and **2-amido-iso-phthalic acids** are formed from 2-nitro-m-xylol (B. **39**, 73). **4-Chloro-iso-phthalic acid**, m.p. 294°; **4-acetamido-iso-phthalic acid**, m.p. 289°; and **4, 6-diamido-iso-phthalic acid** are obtained from chloro-, acetamido-, and diacet-amido-m-xylol, by oxidation with permanganates (B. **36**, 1799, 1803; C. 1909, II. 1234).

Tetrachloro-, **tetrabromo-**, and **tetraiodo-phthalic acids** melt at 181°, 290°, and 310° (B. **29**, 1632). **Tetra-amido-iso-phthalic acid** $C_6(NH_2)_4(COOH)_2$ has been obtained by way of the iso-purpuric acid, which is probably the dinitrile of a dinitro-hydroxylamino-oxy-iso-phthalic acid.

Homologous Iso-phthalic Acids.—There are four theoretically possible methyl-iso-phthalic acids, of which *uvitinic acid* may be mentioned.

Uvitinic acid, mesidic acid, 5-*methyl-iso-phthalic acid* $CH_3[5]C_6H_3[1,3](CO_2H)_2$, melting at 287°, is obtained by oxidising mesitylene with dilute nitric acid. Synthetically, it has been prepared from pyro-racemic acid. In this reaction a condensation product resembling an aldol is first formed from two molecules pyro-racemic acid by boiling with baryta water or, better, with NaHO. This product is para-pyro-racemic acid; two molecules of this condense, with elimination of oxalic acid and water, to form methyl-dihydro-trimesinic acid, which on prolonged boiling with baryta water, or with concentrated H_2SO_4, splits off CO_2 and 2H atoms and passes into *uvitinic acid* (Latin *uva*, a grape) (Wolff, **305**, 125):



If a mixture of pyro-racemic acid and propyl- or iso-butyl-aldehyde is used, we obtain **5-ethyl** and **5-iso-propyl-iso-phthalic acid** (Döbner, B. **23**, 377; **24**, 1746). Chromic acid oxidises these to trimesinic acid.

Distilled with lime, uvitinic acid at first yields meta-toluic acid, then toluol.

Xylidic acid, *4-methyl-iso-phthalic acid* $CH_3[4]C_6H_3[1, 3](CO_2H)_2$, melting at 282°, is obtained by oxidising pseudo-cumol, xylic acid, and iso-xylic acid with dilute nitric acid. Potassium permanganate oxidises it to trimellitic acid.

2-Mesityl-iso-phthalic acid, m.p. 235°, results from the reduction of 2, 6-dicarbon-phenyl-glyoxylic acid with phosphorus and HI (B. **29**, R. 283).

Oxy-iso-phthalic acids are obtained by the same methods from oxy-benzoic acids and aldehyde-oxy-benzoic acids as the latter are got from phenols and phenol-aldehydes. Amido- and sulpho-carboxylic acids also serve as foundation material (B. **16**, 1966; **25**, R. 9).

2-Oxy-, 4-oxy-, and **5-oxy-iso-phthalic acids** melt at 243°, 305°, and 288° respectively. The 4-oxy-iso-phthalic ethyl ester, m.p. 57°, is formed in small quantity in a peculiar condensation process during the action of sodium ethylate free from alcohol upon glutaconic acid ester (B. **37**, 2117).

5, 2-Nitro-oxy-iso-phthalic acid, m.p. 214°, from nitro-malonic aldehyde and acetone-dicarboxylic acid (C. 1900, II. 561).

Dioxy-iso-phthalic acid, reso-dicarboxylic acid, m.p. 305°, see B. **32**, 2796.

Oxy-uvitinic Acids.—Mention may be made of **4-oxy-uvitinic acid** $(CH_3)[5](HO)[4]C_6H_2[1, 3](CO_2H)_2$, produced by the action of chloroform, chloral, or trichloro-acetic ester upon sodium aceto-acetic ester (A. **222**, 249). Methenyl-bis-acetic acid ester (Vol. I.) is an intermediate link (A. **297**, 11).

Terephthalic acid, *benzol-p-dicarboxylic acid* $C_6H_4[1, 4](CO_2H)_2$, sublimes without melting. Iso-phthalic acid was obtained from m-derivatives of benzene; in a similar manner terephthalic acid is formed from p-di-derivatives: p-xylol, p-toluic acid, p-dicyano-benzol, p-cyano-benzoic acid, p-dibromo-benzol, etc. It is obtained in small quantities by the action of Mg and CO_2 upon p-dibromo-benzol (B. **38**, 3796).

The best course to pursue in forming terephthalic acid is to oxidise carraway oil (a mixture of cymol and cuminol) with chromic acid; or it may be prepared from p-toluidin (B. **22**, 2178).

Terephthalic acid is almost perfectly insoluble in water, alcohol, and ether. When reduced it yields di-, tetra-, and hexahydro-terephthalic acids. It forms no anhydride.

The **barium salt** $C_8H_4O_4Ba+4H_2O$ is very slightly soluble in water. The **methyl ester** melts at 140°.

The **chloride** melts at 78° and boils at 259°. The **amic acid** melts at 214°. The **dihydrazide** melts above 300°. The **diazide** $C_6H_4[1, 4](CON_3)_2$ melts at 110° (B. **29**, R. 987).

Terephthalic di-super-acid (?) $C_6H_4[1, 4](COOOH)_2$, in rather insoluble explosive needles, from terephthalyl chloride with alkaline H_2O_2, is precipitated by CO_2 from the alkaline solution as a mono-sodium salt; its **ethyl ester** $C_6H_4(CO_2.OC_2H_5)_2$, m.p. 37°, from tere-

phthalyl chloride with barium ethyl peroxide $Ba(O.OC_2H_5)_2$ (B. **34,** 766).

p-Cyano-benzoic acid $CN[4]C_6H_4CO_2H$, from p-amido-benzoic acid, melts at 214°.

p-Dicyano-benzol $C_6H_4[1, 4](CN)_2$ melts at 215°.

Mononitro-terephthalic acid melts at 259°.

It, and **sulpho-terephthalic acid,** are produced in the nitration and sulphonation of terephthalic acid. **2, 3-, 2, 6-,** and **2, 5-Dinitro-phthalic acids** are also known (B. **28,** 81). **2, 5-Diamido-terephthalic acid** $(NH_2)_2[2, 5]C_6H_2[1, 4](COOH)_2$ is infusible; its diethyl ester is produced by the oxidation of di-imino-succinyl-succinic ester with bromine. Like anthranilic acid, this acid, which contains the same grouping doubled, is capable of forming numerous o-condensation products (C. 1907, II. 542). Consult B. **29,** 1625, 2833, for **tetrachloro-, tetrabromo-** and **tetraiodo-terephthalic acids.**

Alkyl-terephthalic Acids.—The oxidation of pseudo-cumol and durol gives rise to **4-methyl-terephthalic acid, α-xylidic acid,** melting at 282°, and to **2, 5-dimethyl-terephthalic acid, β-cumidic acid** (B. **19,** 2510).

Oxy-terephthalic Acids.—**Oxy-terephthalic acid** has been obtained from nitro-terephthalic acid. It sublimes without melting. **3, 5-Dioxy-terephthalic acid** is the most interesting of the three possible dioxy-terephthalic acids. Mention is made of it because of its connection with succinyl-succinic ester. Its **diethyl ester** may be prepared by withdrawing two hydrogen atoms from succinyl-succinic ester by means of bromine or PCl_5 (B. **22,** 2107), or by the action of sodium ethylate upon dibromo-aceto-acetic ester (A. **219,** 78).

2, 5-Dioxy-terephthalic acid $(HO)_2C_6H_2(CO_2H)_2+2H_2O$ crystallises from alcohol in yellow flakes. Ferric chloride imparts a deep-blue coloration to its solution. When rapidly distilled it decomposes into two molecules of carbon dioxide and hydroquinone.

2, 5-Dioxy-terephthalic ethyl ester crystallises in two distinct forms at the ordinary temperature in *yellowish-green prisms* or plates; at higher temperatures in *colourless flakes.* It also sublimes in the latter form. It melts at 133°. In most of its reactions the ester conducts itself like an hydroxyl derivative. It does not combine with hydroxyl-amine or phenyl-hydrazin, and with sodium and alkyl iodides yields dialkyl ether. It, however, does not react with phenyl cyanate (B. **23,** 259), and shows some analogies with succino-succinic ester. Hence, it is considered a quinone- or diketo-derivative:

$$C_2H_5O_2C.C\begin{matrix}\diagup C(OH)—CH \diagdown \\ \diagdown CH=C(OH) \diagup\end{matrix}C.CO_2C_2H_5 \quad \text{or} \quad C_2H_5O_2C.C\begin{matrix}\diagup CO—CH_2 \diagdown \\ \diagdown CH_2—CO \diagup\end{matrix}C.CO_2C_2H_5.$$

Dioxy-terephthalic ester, by reduction (boiling with zinc and hydrochloric acid in alcoholic solution), is again changed to succinyl-succinic ester (B. **19,** 432; **22,** 2169). A dihydroxamic acid is formed with hydroxylamine hydrochloride; **tetrahydro-dioxy-terephthalic acid** is produced at the same time (B. **22,** 1280). The different physical modifications of the ester and analogous compounds, according to Hantzsch, correspond to two desmotropic conditions—the coloured variety agreeing with the quinone formula, while the colourless corresponds to the hydroxyl formula (B. **22,** 1294). However, the colour cannot be regarded as a certain criterion for the distinction of the

ketone from the hydroxyl form. Even chemical reactions do not prove that desmotropic forms can be accepted (Nef, B. **23,** R. 585; Goldschmidt, B. **23,** R. 260).

Succinyl-succinic acid, whose ester, by the removal of hydrogen, yields 2, 5-dioxy-terephthalic ester, will be discussed in connection with the hydro-aromatic compounds.

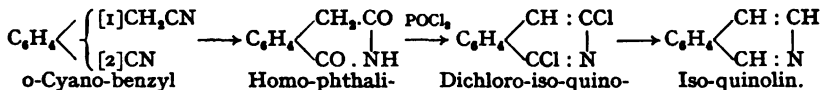
Trioxy-dicarboxylic Acids.—Phloro-glucin-dicarboxylic ester, whose formation by the condensation of three molecules sodium-malonic ester was mentioned in the discussion of benzene ring formations, is dealt with as a derivative of triketo-cyclo-hexane among the hydro-aromatic compounds.

Gallo-carboxylic acid, *trioxy-o-phthalic acid* $(HO)_3[3, 4, 5]C_6H(CO_2H)_2$, melts at 270° with decomposition. It may be prepared from pyrogallol by heating it to 130° with ammonium carbonate. Pyrogallo-carboxylic acid is formed at the same time (B. **18,** 1876).

(*b*) **Aromatic Dicarboxylic Acids** *containing* $1CO_2H$ *in the nucleus and* $1CO_2H$ *in the side chain.*—The three α-homo-phthalic acids, or phenyl-acetic-carboxylic acids, are known. The o-acid readily forms heterocyclic derivatives.

Phenyl-aceto-o-carboxylic acid, *o-α-homo-phthalic acid* $CO_2H[2]C_6H_4CH_2.CO_2H$, melting at 175°, with the elimination of water, may be obtained by fusing gamboge with caustic potash (B. **19,** 1654); by oxidising indene with $KMnO_4$ (B. **32,** 29); by reducing phthalonic acid with HI (B. **31,** 375); and by saponification of its nitriles. Its *anhydride* melts at 141°. On heating, it splits off CO and becomes hydro-diphthal-lactonic acid (B. **31,** 376).

o-Homo-phthalimide, melting at 233°, is produced when the ammonium salt is heated, and when acids act upon the dinitrile. In the latter case o-cyano-phenyl-acetic acid, produced at first, rearranges itself into homo-phthalimide, just as o-cyano-benzoic acid yields phthalimide (B. **23,** 2478). It is rather remarkable that o-homo-phthalimide, when heated with phosphorus oxy-chloride, yields *dichloro-iso-quinolin*, which becomes *iso-quinolin* when further heated with hydriodic acid (B. **27,** 2232, 2492):



o-Cyano-benzyl cyanide — Homo-phthalimide — Dichloro-iso-quinolin — Iso-quinolin.

Homo-phthalimide is directly converted into iso-quinolin when it is heated with zinc dust.

The hydrogen atoms of the CH_2 groups are replaced by two alkyls when homo-phthalimide is heated with caustic potash and alkyl iodides. *Mono*-alkyl-o-benzyl cyanides yield mono-alkyl-homo-phthalimides, which rearrange themselves in the same manner as homo-phthalimide into *alkyl-iso-quinolins* (B. **20,** 2499).

ω-Cyan-o-toluic acid $CO_2H[2]C_6H_4CH_2CN$ melts with decomposition at 116°. Its potassium salt is obtained from phthalide and potassium cyanide (A. **233,** 102).

o-Cyano-benzyl cyanide, *o-β-homo-phthalo-nitrile* $CN[2]C_6H_4CH_2CN$, melting at 81°, is obtained from o-cyano-benzyl chloride. Caustic potash and alkylogens effect the replacement of an hydrogen atom in the

methylene group by an alcohol radicle (see Homo-phthalimide). Acetyl chloride converts it into **ψ-diacetyl-o-cyano-benzyl cyanide** $CN.C_6H_4C(CN):C(CH_3)OCOCH_3$, which may be rearranged into 3-methyl-iso-quinolin (B. **27,** 2232).

Homo-iso-phthalic acid and **homo-terephthalic acid** melt at 185° (B. **36,** 3611). Both sublime. **m-** and **p-Cyano-benzyl cyanides** melt at 88° and 100° (B. **24,** 2416). The *dinitrile*, and the two *nitrile-* and *amine*-acids, the two possible *amido-nitriles*, and the *diamide* of homo-terephthalic acid have been prepared (B. **22,** 3207; **26,** R. 89, 602).

o-Hydro-cinnamic-carboxylic acid $CO_2H[2]C_6H_4CH_2CH_2CO_2H$ melts at 165°. It is formed by oxidising *tetrahydro-β-naphthyl-amine* with potassium permanganate, and by the reduction of dihydro-iso-cumarin carboxylic acid (B. **26,** 1841), as well as from o-carbo-phenyl-glyceric-acid-δ-lactone (B. **25,** 888). It yields α-hydrindone (B. **26,** 708) upon dry distillation.

o-Cyano-benzyl-acetic ester, cyano-hydro-cinnamic ester $CN[2]C_6H_4[1]CH_2.CH_2.CO_2C_2H_5$, melting at 98°, is produced by the rearrangement of the product resulting from the action of aceto-acetic ester, or malonic ester, and sodium ethylate upon cyano-benzyl chloride (B. **22,** 2017). Concentrated hydrochloric acid converts it into α-hydrindone (*q.v.*): $C_6H_4\langle\begin{matrix}CH_2\\CO\end{matrix}\rangle CH_2$.

Phenyl-butyric-o-carboxylic acid $CO_2H[2]C_6H_4CH_2.CH_2.CH_2.CO_2H$ melts at 138° (B. **18,** 3118).

(*c*) **Aromatic Dicarboxylic Acids,** having both carboxyls in different side-groups.

o-, m-, and **p-Phenylene-diacetic acids** $C_6H_4(CH_2CO_2H)_2$, melting at 150°, 170°, and 244°, have been obtained from the xylylene cyanides (B. **26,** R. 941). o-Phenylene-diacetic acid has also been prepared by oxidising dihydro-naphthalene (*q.v.*). Its calcium salt yields β-hydrindone upon distillation (*q.v.*) (B. **26,** 1833).

o-Phenylene-aceto-propionic acid $C_6H_4(CH_2.COOH)[2](CH_2.CH_2COOH)$, m.p. 139°, is obtained from β-oxy-α-naphthoic acid, by rupture of the ring, effected by sodium and amyl alcohol, just as pimelic acid is formed from salicylic acid. It reverts to β-keto-tetrahydro-naphthalene when its calcium salt is distilled (B. **28,** R. 745).

o-, *m-*, and *p-Phenylene-dipropionic acids* $C_6H_4(CH_2.CH_2.CO_2H)_2$, m.p. 161°, 146°, and 223°, are formed from xylylene-dimalonic acids (B. **19,** 436; **21,** 37). Also **p-phenylene-di-iso-butyric acid** $C_6H_4[CH_2CH(CH_3)COOH]_2$, m.p. 169°, from p-xylylene-dimethyl-malonic acid (B. **34,** 2789).

(9) Aldehydo-dicarboxylic Acids.

2-Aldehydo-iso-phthalic acid, m.p. 176°, results from heating 2, 6-dicarbo-phenyl-glyoxylic acid (B. **26,** 1767; **30,** 695).

5-Aldehydo-4-oxy- and **5-aldehydo-2-oxy-iso-phthalic acids** are formed from the corresponding oxy-iso-phthalic acids by means of chloroform and caustic potash (B. **11,** 793).

(10) Tricarboxylic Acids.

The three isomeric benzene-tricarboxylic acids $C_6H_3(CO_2H)_3$ are known. **Trimesic acid, (1, 3, 5)-benzol-tricarboxylic acid,** melts about

300°, and sublimes near 300°. It is formed (1) when mesitylenic and uvitinic acids are oxidised with a chromic acid mixture; (2) by heating mellitic acid with glycerol, or hydro- and iso-hydro-mellitic acid with sulphuric acid. A synthetic method for its production consists in (3) heating benzol-1, 3, 5-trisulphonic acid with potassium cyanide, and saponifying the resulting tricyano-benzol. By the condensation of certain aliphatic substances the acid and its esters have been obtained (1) by polymerising propiolic acid; (2) by the production of its monomethyl ester through the action of caustic potash upon coumalic acid (B. **24,** R. 750); (3) its triethyl ester from formyl-acetic ester.

The intermediate formation of the latter may also explain (4) the synthesis of trimesinic acid ester from formic and halogen-acetic esters with zinc (C. 1898, II. 472).

Its **trimethyl ester** melts at 143°. Its **triethyl ester** melts at 133°.

Trimellitic acid, (1, 2, 4)-*benzol-tricarboxylic acid.*—This is obtained (together with iso-phthalic acid) by heating hydro-pyro-mellitic acid with sulphuric acid, or upon oxidising xylidic acid with potassium permanganate, also from amido-terephthalic acid (B. **19,** 1635). It is prepared most readily (along with iso-phthalic acid) by oxidising colophonium with nitric acid (A. **172,** 97). It melts at 216°, decomposing into water and the anhydride $C_6H_2(CO_2H)(CO)_2O$. The latter melts at 158°.

Hemi-mellitic acid, (1, 2, 3)-*benzol-tricarboxylic acid.*—This is formed on heating hydro-mellophanic acid (below) with sulphuric acid, as well as in the oxidation of phenyl-glyoxyl-dicarboxylic acid, formed from naphthalic acid by action of $KMnO_4$ (B. **29,** 283). It melts at 185° and decomposes into phthalic anhydride. **Triethyl ester,** m.p. 39° (B. **29,** R. 283; **31,** 2084).

Oxy-tricarboxylic acids have been obtained from the sulpho-tricarboxylic acids: **oxy-trimesic acid** (A. **206,** 204); **oxy-trimellitic acid** —see B. **16,** 192.

The condensation of sodium-acetone-dicarboxylic ester into dioxyphenyl-aceto-dicarboxylic ester is dealt with in connection with hydro-aromatic compounds.

(11) Aromatic Tetracarboxylic Acids.

The three isomerides are known. Reduction converts them into tetrahydro-benzol-tetracarboxylic acids (see these).

Pyro-mellitic acid, 1, 2, 4, 5-*benzene-tetracarboxylic acid* $C_6H_2(CO_2H)_4 + 2H_2O$, melts when anhydrous at 264°, and decomposes into water and its anhydride, which is produced when mellitic acid is distilled, or, better, when the sodium salt is subjected to the same treatment with sulphuric acid. The acid is also produced by oxidising durol and durylic acid with potassium permanganate.

The *di-anhydride* $C_6H_2\begin{pmatrix}CO\\CO\end{pmatrix}O\Big)_2$ melts at 286°. The *ethyl ester* $C_6H_2(CO_2.C_2H_5)_4$ melts at 53°.

Dinitro- and **diamido-hydro-mellitic tetra-ethyl esters** melt at 130° and 134°. Nitric acid oxidises the diamido-ether to—

Quinone-tetracarboxylic ester $C_6(O_2)(CO_2.C_2H_5)_4$, crystallising in quinone-yellow needles, melting at 149°. It is odourless, but sublimes quite readily. Zinc reduces it in glacial acetic acid solution to—

Hydroquinone-tetracarboxylic ester $C_6(OH)_2(CO_2.C_2H_5)_4$, crystallising in bright yellow needles, melting at 127°. It may be obtained from sodium-acetone-dicarboxylic ester with iodine (B. **30,** 2570). In alcoholic solution it is reduced by zinc dust and hydrochloric acid to p-diketo-hexamethylene-tetracarboxylic ester (A. **237,** 25).

Prehnitic acid, (1, 2, 3, 4)-*benzene-tetracarboxylic acid* $C_6H_2(CO_2H)_4 + 2H_2O$ melts when anhydrous at 237°, with the formation of an anhydride. It results (together with mellophanic acid and trimesic acid) upon heating hydro- and iso-hydro-mellitic acid with sulphuric acid, also by oxidising prehnitol with potassium permanganate (B. **21,** 907). The salts of this acid form crystals resembling the mineral prehnite.

Mellophanic acid, (1, 2, 3, 5)-*benzene-tetracarboxylic acid,* melts at 238°, with anhydride formation. It is formed by the oxidation of iso-durol with $KMnO_4$; see Prehnitic acid.

(12) Aromatic Pentacarboxylic Acid.

Benzene-pentacarboxylic acid $C_6H(CO_2)H_5 + 6H_2O$ decomposes when it is melted. It is produced by oxidising pentamethyl-benzene with permanganate (B. **17,** R. 376). Also from charcoal with concentrated sulphuric acid (C. 1901, II. 108).

(13) Aromatic Hexacarboxylic Acid.

Mellitic acid $C_6(CO_2H)_6$. When heated it melts and decomposes into water, carbon dioxide, and pyro-mellitic anhydride.

Honey-stone, found in some lignite beds, is an aluminium salt of mellitic acid, crystallising in large quadratic pyramids of bright yellow colour (B. **10,** 566).

An interesting formation of mellitic acid is that whereby pure carbon (graphite, charcoal, etc.) is oxidised with an alkaline solution of potassium permanganate. Another is when the carbon is applied as positive electrode in electrolysis (B. **16,** 1209), and also the oxidation of hexamethyl-benzol with $KMnO_4$.

As hexamethyl-benzol can be synthesised, this latter method of formation would be a synthesis of mellitic acid.

Mellitic acid crystallises in fine silky needles, readily soluble in water and alcohol. It is very stable, and is not decomposed by acids, by chlorine or by bromine, even upon boiling. It yields benzene when distilled with lime.

History.—Klaproth (1799) discovered mellitic acid by boiling honey-stone for a long period with water, and named it honey-stone acid. In 1870 Baeyer proved that mellitic acid was nothing more than benzol-hexacarboxylic acid, in that, by heating with lime, he obtained benzene, and by reduction found hexahydro-mellitic acid (A. suppl., **7,** 1).

Salts and Esters.—The **barium salt** $C_{12}Ba_3O_{12} + 3H_2O$ is insoluble in water. The **methyl ester** melts at 187°; the **ethyl ester** melts at 73°.

The **chloride** $C_6(COCl)_6$ melts at 190°.

Mellimide, *paramide* $C_6\left(\begin{matrix}CO\\CO\end{matrix}\!\!>\!NH\right)_3$, is formed in the dry distillation of the ammonium salt. It is a white, amorphous powder, insoluble in water and alcohol. Heated to 200° with water, it is converted into

the tri-ammonium salt of mellitic acid. The alkalies convert paramide into euchroic acid.

Euchroic acid $C_6[(CO)_2NH]_2\begin{cases}CO.OH\\CO.OH\end{cases}$ crystallises in colourless prisms. Heated with water to 200°, it yields mellitic acid. Nascent hydrogen changes euchroic acid to *euchrone*, a dark-blue precipitate, which reverts to colourless euchroic acid upon exposure. Euchrone dissolves with a dark-red colour in alkalies.

3. Aromatic Polyalcohols, containing more than one Hydroxyl Group in the same Side Chain, and their Oxidation Products.

Of the aromatic polyalcohols, having the hydroxyl groups attached to different carbon atoms of the same side chain, it is only the glycols, and their oxidation products, which have been studied in any sense completely. A more detailed classification of the polyhydric alcohols and their oxidation products is therefore unnecessary; the compounds belonging here will, for practical considerations, be included with the glycols and their oxidation products.

(1) Phenyl-glycols and Phenyl-glycerin.

Phenyl-glycols are produced (1) from the dibromides or bromo-hydrins of the olefin-benzols with potassium carbonate or baryta water; (2) by gentle oxidation of the olefin-benzols with potassium permanganate; (3) by nuclear synthesis in the action of alkyl-magnesium haloids upon aromatic oxy-acid esters and oxy-ketones, *e.g.* $C_6H_5CH(OH)CO_2R \xrightarrow{2CH_3MgI} C_6H_5CH(OH).C(OH)(CH_3)_2$. On heating with dilute sulphuric acid the 1, 2-phenyl-glycols split off water and form aldehydes and ketones, the primary-secondary and primary-tertiary glycols becoming aldehydes without transposition, and the di-secondary and secondary-tertiary glycols becoming ketones, or aldehydes, with migration of the phenyl group (Tiffeneau, C. 1907, I. 1577).

Styrolene alcohol $C_6H_5.CH(OH).CH_2.OH$, *phenyl-glycol*, melts at 67°, boils at 273°, and is obtained from styrol dibromide by the action of a potash solution. Dilute nitric acid oxidises it to *benzoyl-carbinol* and *benzoyl-formic acid* (A. **216**, 293).

Heated with dilute sulphuric acid, it becomes phenyl-acetaldehyde. By the action of 65 per cent. sulphuric acid two molecules are condensed to β-phenyl-naphthalin (*q.v.*). Methylene ether, b.p. 218°, from phenyl-glycol and formaldehyde (B. **32**, 568).

Sym. phenyl-methyl-glycol $C_6H_5CH(OH).CH(OH).CH_3$, α-modification, m.p. 57°, β-modification, m.p. 93°. This glycol occurs, like hydro-benzoïn, in two modifications, generated from the corresponding dibromide (from n-propyl-benzol). Both modifications, on boiling with dilute H_2SO_4, yield phenyl-acetone, and, on oxidation with HNO_3, phenyl-methyl-glyoxal (B. **43**, 849).

Unsym. phenyl-methyl-glycol $C_6H_5(CH_3)COH.CH_2OH$, m.p. 41°, b.p.$_{26}$ 161°, by methods 1 and 3; yields on heating with dilute H_2SO_4 hydratropic aldehyde (C. 1907, I. 1578).

1-Phenyl-2, 3-propylene-glycol $C_6H_5CH_2.CH(OH).CH_2(OH)$, b.p.$_{12}$ 163°, and **1-phenyl-3, 4-butylene-glycol** $C_6H_5CH_2.CH_2.CH(OH).CH_2(OH)$,

b.p.$_{14}$ 178°, are formed by the action of phenyl- and benzyl-magnesium bromide respectively, upon glycerin-α-monochloro-hydrin (C. 1905, II. 1752; 1907, I. 1033).

Sym. dimethyl- and **diethyl-phenyl-glycol** $C_6H_5CH(OH).C(OH)R_2$, m.p. 63° and 78°, by method 3. On heating with dilute H_2SO_4 they pass into dimethyl- and diethyl-phenyl-acetaldehyde respectively, with "phenyl migration" (C. 1909, I. 1335).

Phenyl-butylene-glycol $C_6H_5CH(OH)CH_2.CH_2.CH_2(OH)$, melting at 75°, is obtained by reduction from benzoyl-propionic aldehyde and benzoyl-propyl alcohol.

Phenyl-iso-propyl-ethylene-glycol $C_6H_5CH(OH)CH(OH)CH(CH_3)_2$, melting at 81° and boiling at 286°, results from the reduction of benz-aldehyde and iso-butyl-aldehyde.

Methylene-m, p-dioxy-benzyl-glycol $[CH_2O_2][3, 4]C_6H_3CH_2CH(OH)CH_2(OH)$, melting at 82°, and **methylene-m, p-dioxy-phenyl-ethylene-methyl-glycol** $(CH_2O_2)[3, 4]C_6H_3.CH(OH).CH(OH).CH_3$, melting at 101°, result from the action of $KMnO_4$ (B. **24,** 3488) upon *safrol* and *iso-safrol.* The corresponding glycols, melting at 68° and 88°, are obtained from *anethol, eugenol,* and *iso-eugenol.*

Styrcrine $C_6H_5.CH(OH).CH(OH).CH_2.OH$, a rubber-like mass, is obtained from styrone bromide and cinnamic alcohol, $C_6H_5.CHBr.CHBr.CH_2.OH$, with potassium permanganate (B. **24,** 3491).

Phenyl-alkylene oxides are obtained from the halogen hydrins of the phenyl-glycols by treatment with alkali. On heating by themselves, or by warming with dilute sulphuric acid, they are converted into aldehydes or ketones (C. 1905, II. 1628).

Styrol oxide, *phenyl-ethylene oxide* $C_6H_5\overline{CH\ O.CH_2}$, b.p. 191°, from phenyl-glycol-iodo-hydrin and caustic potash; gives phenyl-acetaldehyde and diphenyl-diethylene oxide with dilute acids (C. 1908, I. 1776).

Unsym. phenyl-methyl-ethylene oxide $C_6H_5(CH_3)\overline{C.O.CH_2}$, b.p.$_{17}$ 85°–88°, converted into hydratropic aldehyde with dilute acids or on heating alone (B. **38,** 1969).

Sym. phenyl-methyl-ethylene oxide $C_6H_5\overline{CH.O.CH}.CH_3$, b.p.$_{15}$ 93°.

γ-Phenyl-propylene oxide $C_6H_5CH_2\overline{CH.O.CH_2}$, b.p.$_{15}$ 94°–98° (C. 1905, II. 237).

Haloid Esters of the Phenyl-glycols.—(*a*) **Halogen Hydrins.**—Of particular interest is the behaviour of the halogen hydrins of phenyl-glycols in the presence of silver nitrate and mercuric oxide respectively. While caustic alkalies transform them, as above mentioned, into the corresponding alkylene oxides with elimination of hydrogen haloids, the action of silver nitrate, or mercuric oxides, with the same elimination, produces aldehydes and ketones respectively, with migration of the phenyl group (Tiffeneau, C. 1907, I. 1577):

$$C_6H_5CH(OH).CHI.CH_3 \xrightarrow{-HI} OCH.CH\begin{matrix}CH_3\\C_6H_5\end{matrix}$$

$$\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>\!C(OH).CH_2I \xrightarrow{-HI} CH_3CO.CH_2.C_6H_5.$$

That in these transpositions the splitting off of HI probably takes place at the same carbon atom, is indicated by the fact that the iodo-

hydrin ethers, treated with mercuric oxide, also pass into phenyl-vinyl ethers with migration of the phenyl (C. 1908, I. 828):

$$CH_3OC_6H_4CH(OC_2H_5).CHI.CH_3 \xrightarrow{HI} C_2H_5OCH : C\begin{matrix}CH_3\\C_6H_4OCH_3\end{matrix}.$$

α-Phenyl-ethylene-β-iodo-hydrin $C_6H_5CH(OH).CH_2I$, b.p.$_{18}$ 148°–152°, with decomposition into HI and aceto-phenone; formed from styrol (*q.v.*) with iodine, and yellow HgO, in aqueous etheric solution. The isomeric **α-phenyl-ethylene-α-iodo-hydrin** $C_6H_5CHI.CH_2(OH)$, m.p. 79°, is obtained by the attachment of HI to styrol oxide (C. 1908, I. **42**, 1777).

β-Phenyl-propylene-glycol-α-chloro-hydrin $C_6H_5(CH_3)C(OH).CH_2Cl$, b.p.$_{17}$ 124°, is formed by the action of C_6H_5MgBr upon chloro-acetone and of CH_3MgI upon ω-chloro-aceto-phenone, or by the attachment of hypo-chlorous acid to iso-propenyl-benzol.

Bromo-hydrin, b.p.$_{19}$ 141°. **Iodo-hydrin,** b.p.$_{12}$ 145° (C. 1907, I. 1200).

Benzyl-glycol-chloro-hydrin $C_6H_5CH_2CH(OH).CH_2Cl$, b.p.$_{27}$ 153°, by the action of C_6H_5MgBr upon epi-chloro-hydrin (C. 1908, I. 830).

(*b*) **Dihaloids.**—These are formed by the attachment of halogens to olefin-benzols. In the dibromides of the olefin-phenols, and their ethers, as in the oxy-phenyl (or pseudo-phenol) haloids, the bromine atom occupying the α-position towards the phenyl group is very mobile, and by treatment with aqueous acetone, sodium alcoholate, potassium acetate, aniline, etc., it can be easily replaced by the groups OH, OC_2H_5, $OCOCH_3$, or NHC_6H_5. The action of concentrated nitric acid upon these dibromides is peculiar, the α-bromine atom migrating to the nucleus, and α-ketones being formed. Thus anethol dibromide yields $(CH_3O)BrC_6H_3CO.CHBr.CH_3$ (B. **38**, 3458).

Styrol dichloride, α, *β-dichloro-ethyl-benzol* $C_6H_5CHClCH_2Cl$, liquid. **Styrol dibromide,** m.p. 60°. **Anethol dibromide** $CH_3OC_6H_4CHBr.CHBrCH_3$, m.p. 65°. **Iso-safrol dibromide** $CH_2(O)_2C_6H_3CHBr.CHBrCH_3$, liquid (B. **28**, 2719).

Phenyl-oxalkyl-amines.—These compounds have attained great importance since it has been found that adrenalin, a body of great physiological significance, belongs to this class of compounds. These substances are obtained (1) from phenyl-glycol halogen hydrins by transformation with amines; (2) by reduction of the aromatic amido-ketones; and (3) of the oxy-acid nitriles.

Phenyl-oxethyl-amine $C_6H_5CH(OH).CH_2NH_2$. The chlorohydrate melts at 177°, the picrate at 154°. By reduction of mandelic acid nitrile with sodium amalgam (C. 1908, I. 430).

1-Methyl-amido-2-phenyl-2-propanol $C_6H_5(CH_3)C(OH).CH_2NHCH_3$, b.p.$_{33}$ 137°, and **1-methyl-amido-3-phenyl-2-propanol** $C_6H_5CH_2.CH(OH).CH_2NHCH_3$, b.p.$_{22}$ 148°, by method 1 (C. 1905, I. 232).

Ephedrin $C_6H_5CH(OH).CH(NHCH_3).CH_3$(?), m.p. 39°; chlorohydrate, m.p. 210°, has been isolated from *Ephedra vulgaris* besides the stereo-isomeric (?) **pseudo-ephedrin** (B. **22**, 1823). By heating with HCl, or acetic anhydride, they can be converted into each other (C. 1910, II. 1480). Both chlorohydrates decompose in dry heat into methyl-amine chloride and propio-phenone (C. 1909, I. 1705).

3, 4-Dioxy-phenyl-oxethyl-amine $(OH)_2[3, 4]C_6H_3[1]CH(OH).CH_2$

NH_2, white crystalline meal, melting at 191° with decomposition, is formed by the reduction of amido-aceto-pyro-catechin or of proto-catechin-aldehyde-cyano-hydrin with sodium amalgam (C. 1908, I. 430).

Adrenalin, *suprarenin* $(HO)_2[3,4]C_6H_3[1]CH(OH).CH_2NHCH_3$, m.p. about 216° with decomposition, was isolated in 1901 by J. Takamine (C. 1901, II. 1354) from the extract of suprarenal capsules, whence the name (Latin *renes*, kidneys). It is of great physiological and pharmaceutical importance, since even in very small quantities it produces a great increase of the blood-pressure and a contraction of the peripheral blood-vessels.

Adrenalin is optically active, its specific rotatory power for D being −53·5°. It dissolves with difficulty in water and the organic solvents, but easily in acids and alkalies. On heating with NaHO, it decomposes with elimination of methyl-amine. Methylation, and subsequent oxidation, produce veratric acid. This settles its constitution, which is confirmed by synthesis. The latter starts from chloraceto-pyro-catechin (obtained from pyro-catechin and chloracetyl chloride), which yields inactive adrenalin by transformation with methyl-amine and reduction with Al amalgam (F. Stolz, B. **37,** 4149; C. 1905, I. 315):

$$C_6H_4\begin{cases}OH\\OH\end{cases} \longrightarrow C_6H_3\begin{cases}[1]CO.CH_2Cl\\[3]OH\\[4]OH\end{cases} \longrightarrow C_6H_3\begin{cases}CO.CH_2NHCH_3\\OH\\OH\end{cases} \longrightarrow C_6H_3\begin{cases}CH(OH).CH_2NHCH_3\\OH\\OH\end{cases}$$

The racemic adrenalin so obtained can be decomposed into its optically active components by means of its tartrates. The lævo-modification agrees in all its properties with the natural product (*Z. physiol. Ch.* **58,** 189). It is remarkable that the physiological effects of lævo-rotatory adrenalin are about fifteen times as great as those of the dextro-rotatory modification.

A number of derivatives of adrenalin have been obtained synthetically, and some of them show similar physiological effects.

Adrenalin-dimethyl ether $(CH_3O)_2C_6H_3CH(OH).CH_2NHCH_3$, m.p. 104°, and **adrenalin-methylene ether** $CH_2(O)_2C_6H_3CH(OH).CH_2NHCH_3$, m.p. 96°, are obtained from the bromo-hydrins of the corresponding olefin-phenol ethers, by transformation with methyl-amine (C. 1910, I. 2115).

(2) Phenyl-alcohol Aldehydes.

Just as two molecules of acetaldehyde condense to aldol, so the nitro-benzaldehydes combine with acetaldehyde, under the influence of very dilute sodium hydroxide (2 per cent.) to the corresponding aldols, the **nitro-phenyl-lactic acid aldehydes** $NO_2C_6H_4CH(OH)CH_2CHO$, which unite with an additional molecule of acetaldehyde. Dehydrating agents, like acetic anhydride, convert them into the corresponding nitro-cinnamic aldehydes (B. **18,** 719).

o-Oxy-mandelic aldehyde, o-oxy-phenyl-glycol aldehyde $HO[2]C_6H_4CH(OH)CHO$, m.p. 64°, has been obtained from cumarone dichloride by splitting up with sodium acetate (A. **313,** 96).

Phenyl-glycerin aldehyde $C_6H_5CH(OH)CH)OH(CHO$; its dimethyl-acetal, m.p. 80°, is formed by oxidation of cinnamic aldehyde-acetal with permanganate; phenyl-hydrazone, m.p. 170° (B. **31,** 1995).

Phenyl-tetrose $C_6H_5.CH(OH)CH.OH.CH(OH).COH$ is a colourless syrup resulting from the reduction of phenyl-trioxy-butyric acid lactone (*q.v.*). Its *phenyl-hydrazone* melts at 154°.

(3) Phenyl Ketols.

Aceto-phenone alcohol, *benzoyl-carbinol* $C_6H_5.CO.CH_2.OH$, crystallises from water and dilute alcohol in large, brilliant flakes, which contain water of crystallisation, and melt at 73°. It crystallises from ether in shining anhydrous plates, and melts at 85°. It is produced in the oxidation of phenyl-glycol, and from its chloride, ω-chloraceto-phenone, by its conversion into acetate and saponification with potassium carbonate (B. **16,** 1290; **89,** 2294). Also from ω-diazo-aceto-phenone by means of dilute H_2SO_4; and by the action of benzene and $AlCl_3$ upon acetyl-glycolic acid chloride (A. **368,** 89).

When distilled it decomposes, with formation of bitter-almond oil. Being a ketone, it forms crystalline compounds with primary alkaline sulphites. With hydroxylamine it forms an oxime, melting at 70°; with phenyl-hydrazin, a phenyl-hydrazone, m.p. 112°; and further, the osazone of phenyl-glyoxal. Like acetyl-carbinol, it reduces a cold ammoniacal silver or copper solution (forming benzaldehyde and benzoic acid), and is oxidised to mandelic acid (B. **14,** 2100). Nitric acid oxidises it to phenyl-glyoxylic acid. It yields cyano-hydrin with CNH, which then forms α-phenyl-glyceric acid, or atro-glyceric acid (*q.v.*).

Bis-methyl-benzoyl-carbinol $\begin{matrix} C_6H_5C(O.CH_3)—O—CH_2 \\ | \qquad\qquad\quad | \\ CH_2 ———O—C(OCH_3)C_6H_5 \end{matrix}$ (?), melting at 192°, is formed from benzoyl-carbinol with methyl alcohol and hydrochloric acid (B. **28,** 1161).

Benzoyl-carbinol acetate $C_6H_5CO.CH_2.O.COCH_3$ melts at 49° and boils at 270°. The *benzoate* melts at 117°. The *phenyl ether* melts at 72°.

ω-Chloro-aceto-phenone, *phenacyl chloride, benzoyl-carbinol chloride* $C_6H_5COCH_2Cl$, melting at 59° and boiling at 245°, results from the chlorination of boiling aceto-phenone (B. **10,** 1830), as well as from benzene, chloracetyl chloride, and aluminium chloride.

ω-Bromo-aceto-phenone, *phenacyl bromide* $C_6H_5.CO.CH_2Br$, melting at 50°, attacks the mucous membrane quite powerfully. It is obtained from aceto-phenone and bromine, also by heating dibromatro-lactinic acid with water (B. **14,** 1238). An excess of alcoholic ammonia changes it to *iso-indol*—a hydrazin derivative. With methyl-ethyl sulphide it combines to **phenacyl-methyl-ethyl-sulphinium bromide** $C_6H_5COCH_2S(CH_3)(C_2H_5)Br$, which may be split up into optically active components by means of bromo-camphor-sulphonic acid (see unsym. sulphur atom, C. 1900, II. 960). The acid amides and thiamides change the ω-haloid aceto-phenones into *oxazole* and *thiazole* derivatives (*q.v.*). With excess of alcoholic ammonia, phenacyl bromide passes into diphenyl-dihydro-pyrazin.

Gallo-chloro-aceto-phenone $C_6H_2(OH)_3COCH_2Cl$, and **ω-bromo-resaceto-phenone,** containing the hydroxyl group in the ortho-position, part with halogen hydrides, and become cumarone derivatives (B. **30,** 299).

ω-Iodo-aceto-phenone, phenacyl iodide $C_6H_5COCH_2I$, m.p. 30°, from ω-chloro- or bromo-aceto-phenone with potassium iodide (C. 1899, I. 559; B. **32**, 532). It forms with Ag nitrite:

ω-Nitro-aceto-phenone $C_6H_5COCH_2.NO_2$, m.p. 108°. This is also obtained from its dimethyl-acetal $C_6H_5C(OCH_3)_2CH_2.NO_2$, m.p. 56° (B. **36**, 2558). In potash it dissolves to form the salt C_6H_5COCH: NOOK. Stannous chloride reduces it to—

ω-Amido-aceto-phenone $C_6H_5.CO.CH_2.NH_2$ which is unknown in a free condition. The chlorohydrate $C_6H_5.CO.CH_2.NH_2HCl$, melting at 183°, is formed when the iso-nitroso-aceto-phenone is reduced with tin and hydrochloric acid (B. **28**, 254), or by the breaking up of *phthalimino-aceto-phenone* $C_6H_4(CO)_2NHCH_2COC_6H_5$ with concentrated HCl. The free ω-amido-aceto-phenone is unstable, like the α-amido-ketones of the aliphatic series. Liberated from its chlorohydrate with NaHO, or ammonia, it immediately splits off water and passes into *diphenyl-dihydro-pyrazin* $C_6H_5C\begin{matrix}N{-}CH_2\\ CH_2{-}N\end{matrix}CC_6H_5$ which is also obtained, with small quantities of **diphenacyl-amine** $(C_6H_5COCH_2)_2NH$, m.p. 75°, by the action of ammonia upon ω-bromo-aceto-phenone. Heating with HCl regenerates the chlorohydrate. With excess of NaHO it loses water, and easily passes into a base isomeric with diphenyl-dehydro-pyrazin, probably 3, 5-*diphenyl-4-amido-pyrrol* $NH\begin{matrix}CH{=}C.NH_2\\ C(C_6H_5){:}C.C_6H_5\end{matrix}$ (B. **41**, 1127). With sodium nitrite the ω-amido-aceto-phenone chloride yields **ω-diazo-aceto-phenone**, *benzoyl-diazo-methane* $C_6H_5COCH\begin{matrix}N\\ \|\\ N\end{matrix}$, m.p. 50°, which also results from benzoyl-acetone-diazo-anhydride by splitting up with ammonia. Diazo-aceto-phenone, on boiling with dilute H_2SO_4, is decomposed into N_2 and benzoyl-carbinol. With iodine it yields **ω-di-iodo-aceto-phenone** $C_6H_5COCHI_2$; with KCN it forms a **potassium salt of phenacyl-azo-cyanide** $C_6H_5COCH_2N:NCN$, colourless crystals, m.p. 72° with decomposition, which, with H_2SO_4, yields **phenacyl-azo-carbonamide** $C_6H_5.COCH_2N:NCONH_2$, m.p. 217° with decomposition (A. **325**, 141).

ω-Methyl-amido-, dimethyl-amido-aceto-phenone, and **ω-trimethyl-amido-aceto-phenone bromide** $C_6H_5COCH_2N(CH_3)Br$ are generated from phenacyl bromide with mono-, di-, and trimethyl-amine (C. 1899, I. 1284).

ω-Aceto-phenone-anilide, *phenacyl-anilide* $C_6H_5.CO.CH_2NHC_6H_5$, m.p. 93°, from **ω-bromo-aceto-phenone** and aniline (B. **15**, 2467), may be condensed to α-phenyl-indol (B. **21**, 1071, 2196, 2595).

p-Amido-benzoyl-carbinol $NH_2[4]C_6H_4COCH_2OH$, m.p. 165°, is obtained by transforming a body obtained synthetically from acetanilide and chloracetyl chloride by means of $AlCl_3$, viz. p-acetamido-phenacyl chloride $CH_3CONHC_6H_4COCH_2Cl$, m.p. 212° (B. **33**, 2644).

α-Amido-propio-phenone $C_6H_5.CO.CH(NH_2)CH_3$, chlorohydrate, m.p. 183°, by reduction of iso-nitroso-propio-phenone, or from phthalyl-alanyl chloride, benzol, and $AlCl_3$. Like ω-amido-aceto-phenone, the free base liberates water and passes spontaneously into 2, 5-*dimethyl-3, 6-diphenyl-dihydro-pyrazin* $C_6H_5C\begin{matrix}N{-}CH(CH_3)\\ CH(CH_3){-}N\end{matrix}CC_6H_5$, from which HCl generates, besides some of the original amido-ketone, the isomeric

α-amido-α-phenyl-acetone $C_6H_5CH(NH_2)COCH_3$, which may be obtained by reduction of the iso-nitroso-phenyl-acetone (B. **41,** 1146).

Phenyl-acetyl-carbinol $C_6H_5CH(OH)COCH_3$, b.p.$_{40}$ 135°, from α-bromo-benzyl-methyl-ketone $C_6H_5CHBrCOCH_3$ by way of the acetate (C. 1904, I. 24).

α-Benzyl-amido-acetone $C_6H_5CH_2CH(NH_2)COCH_3$ whose chlorohydrate melts at 127°, is formed by reduction of iso-nitroso-benzyl-acetone (B. **40,** 4666).

Corresponding to the nitro-phenyl-lactic aldehydes we have **o-** and **p-nitro-phenyl-lactic ketones,** m.p. 69° and 58°, the condensation products of o- and p-nitro-benzaldehyde and acetone, in the presence of very dilute NaHO. By boiling with water or by excess of NaHO the o-nitro-ketone is converted into *indigo* (*q.v.*) with rejection of acetic acid and water (B. **16,** 1968). See also Nitro-benzylidene-acetones.

ω-Chloraceto-pyro-catechin $(OH)_2[3,4]C_6H_3COCH_2Cl$, m.p. 173°, from pyro-catechin and chloracetyl chloride, yields with methyl-amine **ω-methyl-amido-aceto-pyro-catechin** $(OH)_2C_6H_3COCH_2NHCH_3$, chlorohydrate, m.p. 240° (B. **37,** 4152).

Benzoyl-butyl-carbinol $C_6H_5.CO.[CH_2]_3.CH_2OH$, m.p. 40° (B. **28,** R. 500).

β-Amido-propio-phenone $C_6H_5COCH_2.CH_2NH_2$, chlorohydrate, m.p. 128°, is formed from α-phthalyl-anyl chloride, benzene, and $AlCl_3$. NaHO liberates the free base as an oil (B. **41,** 244).

γ-Amido-butyro-phenone $C_6H_5CO.CH_2.CH_2.CH_2NH_2$ is unstable; it passes spontaneously into *2-phenyl-pyrrolin* $C_6H_5C\begin{matrix}NH—CH_2\\ \| \\ CH—CH_2\end{matrix}$ (B. **41,** 513) with liberation of water. A similar dehydration occurs in **δ-amido-valero-phenone** $C_6H_5COCH_2.CH_2.CH_2.CH_2NH_2$, from phthalimido-valerianic acid, which is easily reduced to *2-phenyl-tetra-hydro-pyridin.* On the other hand, *ε-amido-capro-phenone* $C_6H_5CO[CH_2]_4CH_2NH_2$, whose chlorohydrate melts at 154°, shows no tendency to split off water. The free base is an oil volatile in steam, and has a peculiar odour (B. **41,** 2014).

Triphenyl-acyl-methyl-amine $[C_6H_5COCH_2CH_2]_3N$, chlorohydrate, m.p. 201°, is formed on heating aceto-phenone, AmCl, and formaldehyde solution; on distilling with steam, it decomposes, forming *phenyl-vinyl-ketone* (B. **39,** 2181).

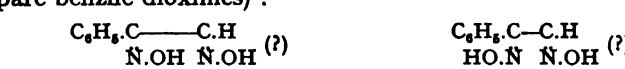
(4) Phenyl-aldehyde Ketones.

α-Ketone-aldehydes. — Phenyl-glyoxal, *benzoyl-formaldehyde* $C_6H_5.CO.CH(OH)_2$, melts at 73°. The anhydrous aldehyde boils at 142° (125 mm.). It has a penetrating odour. It is obtained from its aldoxime, iso-nitroso-aceto-phenone, upon boiling the sodium sulphite derivative with dilute sulphuric acid (B. **22,** 2557). Alkalies convert it into almond acid; potassium cyanide condenses it to benzoyl-formoïn, just as it changes benzaldehyde to benzoïn. It yields quinoxalins with o-diamines.

ω-Dichloro-aceto-phenone $C_6H_5.CO.CHCl_2$ boils at 253° (B. **10,** 531). **ω-Dibromo-aceto-phenone** $C_6H_5.CO.CHBr_2$., m.p. 36° (B. **10,** 2010; A. **195,** 161). **ω-Dibromo-p-iodo-aceto-phenone** (B. **24,** 997). **ω-Dichloro-o-nitro-aceto-phenone** melts at 73° (A. **221,** 328). **ω-Di-**

bromo-o-, m-, and **p-nitro-aceto-phenone** melt at 85°, 59°, and 98° (B. **20,** 2203; **18,** 2240; **22,** 204).

Iso-nitroso-aceto-phenone, *benzoyl-formoxime* $C_6H_5CO.CH(N.OH)$, m.p. 127°, is obtained from aceto-phenone (B. **24,** 1382; **25,** 3459; A. **358,** 56). It forms diphenyl-pyrazin (*q.v.*) by reduction. **Phenyl-glyoxime** $C_6H_5C(NOH).CH(NOH)$ is known in two modifications (compare benzile dioximes):



Phenyl-amphi-glyoxime, m.p. 168° Phenyl-anti-glyoxime, m.p. 180°.

Phenyl-amphi-glyoxime is produced when hydroxylamine acts upon ω-dibromo-aceto-phenone and iso-nitroso-aceto-phenone. When treated in absolute ether with hydrochloric acid gas, it changes to the anti-modification, which reverts to the amphi-modification by recrystallisation from indifferent solvents (B. **24,** 3497). See also Phenyl-furoxane.

α-Phenyl-glyoxal-phenyl-hydrazone $C_6H_5C(NNHC_6H_5)CHO$ (?), m.p. 142°, from phenyl-glyoxal with phenyl-hydrazin, and the **β**-hydrazone $C_6H_5COCH : NNHC_6H_5$, two modifications easily converted into each other, m.p. 138° and 114°, from benzoyl-acetic acid with diazo-benzol (B. **22,** 2557; **34,** 2001).

Phenyl-glyoxal-phenyl-osazone $C_6H_5.C : (N.NH.C_6H_5).CH : (N.NHC_6H_5)$ melts at 152°. (See Benzoyl-carbinol-phenyl-hydrazone, B. **22,** 2258). **Phenyl-glyoxal-methyl-phenyl-osazone** melts at 152° (B. **21,** 2597).

p-Toluic formaldehyde $CH_3C_6H_4CO.CH(OH)_2$ melts at 101° (B. **22,** 2560).

Anthroxan-aldehyde $C_6H_4\begin{cases}[1]C—CHO \\ [2]N\end{cases}>O$, melting at 72°, is formed from o-nitro-phenyl-glycidic acid (B. **16,** 2222) (compare anthranile).

β-Ketone-aldehydes.—*Formyl-aceto-phenone,* or *benzoyl-acetaldehyde,* was formerly regarded as **β**-ketone-aldehyde, in which, as in formyl-acetone, an unsaturated ketol, oxy-methylene-aceto-phenone, is present. This will, therefore, be discussed later in connection with the compounds containing an unsaturated side chain. The sodium salt of oxy-methylene-aceto-phenone and hydroxylamine hydrochloride yield **benzoyl-acetaldoxime** $C_6H_5.CO.CH_2.CH : N.OH$, melting at 86°, which acetic anhydride converts into cyanaceto-phenone and acetyl chloride into the isomeric phenyl-isoxazole.

γ-Ketone-aldehydes. — **Benzoyl-propio-aldehyde** $C_6H_5CO.CH_2.CH_2.CHO$ boils at 245°.

(5) Phenyl-paraffin Diketones.

α-Diketones, or *ortho-diketones,* are produced from their monoximes, the phenyl-iso-nitroso-ketones (compare phenyl-glyoxal) by distillation with dilute acids, or by digesting with amyl nitrite (B. **21,** 2177). **Benzoyl-acetyl** $C_6H_5.CO.CO.CH_3$, boiling at 214°, is a yellow oil with a peculiar odour (B. **21,** 2119, 2176). It is formed by the oxidation of the two stereo-isomeric phenyl-methyl-glycols with NO_3H (B. **43,** 855). **Acetyl-benzoyl-aceto-hydrazone** $CH_3CO.C(NNHCOCH_3)C_6H_5$, m.p. 154°, is dissolved in NaHO to the sodium salt of a pseudo-form (B. **36,** 3187).

α-Oximido-propio-phenone $C_6H_5.CO.C:(NOH).CH_3$, melting at 113°, results from the action of nitrous acid upon methyl-benzoyl-acetic ester, or by the action of diazo-benzol chloride upon an alkaline solution of iso-nitroso-acetone, probably with intermediate formation of a phenyl-azo-aldoxime (B. **40,** 737):

$$CH_3COCH:NOH \longrightarrow [CH_3COC(:NOH).N:NC_6H_5] \longrightarrow CH_3COC(:NOH)C_6H_5.$$

β-Oximido-propio-phenone, *iso-nitroso-phenyl-acetone* $C_6H_5C:(NOH)COCH_3$, from phenyl-acetone, with amyl nitrite and sodium alcoholate.

Phenyl-methyl-glyoxime $C_6H_5C:(NOH)C:(NOH)CH_3$, m.p. 118° (A. **291,** 280). **p-Methoxy-phenyl-methyl-glyoxime** $CH_3O[4]C_6H_4C(NOH).C(NOH)CH_3$, m.p. 206° with decomposition, is formed, beside the corresponding **peroxide**, m.p. 97°, from anethol with nitrous acid (A. **329,** 262).

The β- or *meta-diketones* result, together with aceto-phenone, (1) from the decomposition of the benzoyl-aceto-acetic esters (B. **16,** 2239); further, by (2) a remarkable condensation induced by sodium alcoholate (Claisen, B. **20,** 2178).

The β-diketones behave like the β-diketones of the fatty series. They dissolve in alkalies. This distinguishes them from the other diketones. They are coloured an intense red by ferric chloride. They condense to *isoxazols* with hydroxylamine (B. **21,** 1150). They form pyrazol compounds with phenyl-hydrazin, just like the oxy-methylene-β-ketones.

Benzoyl-acetone, *acetyl-aceto-phenone* $C_6H_5.CO.CH_2.CO.CH_3$, melts at 61°–60°, boils at 260°–262°, and readily volatilises with steam. It is formed from benzoyl-aceto-acetic ester, from ethyl benzoate and acetone, or ethyl acetate and aceto-phenone with sodium ethylate, free from alcohol. See B. **27,** 1571, for the addition of CNH to benzoyl-acetone. See *J. pr. Ch.* 2, **48,** 489, for the action of urea and guanidin.

The Cu-compound of benzoyl-acetone gives, with SCl_2: thio-benzoyl-acetone $S[CH(COCH_3)COC_6H_5]_2$, m.p. 95°; with S_2Cl_2: dithio-benzoyl acetone $S_2[CH(COCH_3)COC_6H_5]_2$, m.p. 118° (C. 1903, II. 243). **o-Nitro-benzoyl-acetone,** m.p. 55° (A. **221,** 332). **Benzoyl-nitro-acetone,** in the form of its oxime $C_6H_5C(NOH).CH(NO_2)COCH_3$, results from benzylidene-acetone when treated with N_2O_3 (B. **36,** 3021).

Propionyl-, butyryl-, iso-butyryl-, and **valeryl-aceto-phenones** boil at 172° (30 mm.), 174° (24 mm.), 170° (26 mm.), and 183° (30 mm.) (B. **20,** 2181).

Phenyl-acetyl-acetone $C_{11}H_{12}O_2=C_6H_5.CH_2.CO.CH_2.CO.CH_3$, boiling at 266°, results from the decomposition of phenyl-acetyl-aceto-acetic ester (B. **18,** 2137).

The following is a γ-diketone:

Aceto-phenone-acetone, *phenacyl-acetone* $C_6H_5.CO.CH_2.CH_2.CO.CH_3$, is obtained from aceto-phenone-aceto-acetic ester. It is a yellow oil, boiling with decomposition (B. **17,** 2756).

Being a γ-diketone, it can split off water and yield phenyl-methyl-furfurane, phenyl-methyl-thio-phene, and phenyl-methyl-pyrrol.

Triketones.—Phenyl-methyl-triketone, phenyl-triketo-butane, b.p.$_{24}$ 138°, is a reddish-yellow oil, combining easily with water to a colourless hydrate melting at 54°–58°. With acetyl-acetone and similar bodies it forms addition products. It reduces copper salts. Phenyl-triketo-

butane was obtained by the disintegration of its **dimethyl-amido-anile** $C_6H_5COC[NC_6H\text{-}N(CH_3)_2]COCH_3$, m.p. 99°, formed from benzoyl-acetone with nitroso-dimethyl-aniline. With diazo-benzol, benzoyl-acetone forms **phenyl-azo-benzoyl-acetone** $C_6H_5COC(HN_2C_6H_5)COCH_3$, m.p. 99°. With HNO_2 it gives **iso-nitroso-benzoyl-acetone** $C_6H_5COC(NOH)COCH_3$, m.p. 125°. This gives, by reduction with zinc and sulphuric acid, benzoyl-amido-acetone, and this again, treated with HNO_2, gives **benzoyl-acetone-diazo-anhydride** $N\langle^{O\text{—}CCH_3}_{N\text{—}CCOC_6H_5}$, m.p. 66°. This diazo-anhydride is split up by ammonia into acetic acid and diaceto-phenone, and by boiling with water and transposition into nitrogen, CO_2 and **benzyl-methyl-ketone** $C_6H_5CH_2COCH_3$; for further transformations, see Heterocyclic compounds: *furo-[a b]-diazols* (A. **325,** 136).

Phenacyl-diacetyl-methane $C_6H_5COCH_2CH(COCH_3)_2$, m.p. 58°, from phenacyl bromide and sodium-acetyl-acetone, is both a 1, 3- and a 1, 4-diketone, and therefore yields both isoxazols and pyrazols, as well as *furfuranes* and *pyrrols* (C. 1902, I. 1164).

Tetraketones.—Benzal-bis-acetyl-acetone $C_6H_5CH[CH(COCH_3)_2]_2$ results from the condensation of benzaldehyde with acetyl-acetone in the presence of piperidin, and has been obtained in the six possible allotropic modifications of the keto- and enol forms with the corresponding *cis-* and *trans-*forms (C. 1900, I. 1099).

(6) Phenyl-paraffin Alcohol Acids.

A. **Monoxy-alcohol Acids.**—Phenyl-alcohol-carboxylic acids, like the aliphatic-alcohol acids, are produced (1) by the reduction of the corresponding ketonic acids; (2) from aldehydes and ketones (B. **12,** 815) by the addition of hydrocyanic acid and the saponification of the α-oxy-acid nitrile; (3) from the corresponding monohalogen acids; (4) from unsaturated monocarboxylic acids, etc.

α- and **β-Oxy-acids.—Almond acid, phenyl-glycollic acid** $C_6H_5.*CHOH.CO_2H$, is isomeric with the cresotinic acids, and the oxy-methyl-benzoic acids, or carbinol-benzoic acids. It contains an asymmetric carbon atom, and therefore, like the lactic acid of fermentation, appears in one inactive, decomposable, and two optically active modifications.

Para-mandelic acid, *inactive mandelic acid,* melting at 118°, is formed (1) from benzaldehyde, prussic acid, and hydrochloric acid (B. **14,** 239, 1965); (2) from benzoyl-formic acid, by reduction with sodium amalgam; and (3) from phenyl-chloracetic acid by boiling it with alkalies (B. **14,** 239), (4) as well as from ω-dibromo-aceto-phenone or phenyl-glyoxal by the action of alkalies:

$$C_6H_5.CO.CHO \longrightarrow C_6H_5.CHOH.CO_2H.$$

The production of alcohol and carboxylic acid, which completes itself extra-molecularly in the action of caustic alkali upon benzaldehyde, in the case of the conversion of phenyl-glyoxal into mandelic acid proceeds intra-molecularly. See below for the formation of para-mandelic acid from lævo- and dextro-mandelic acids.

One hundred parts water at 20° dissolve 15·9 parts of para-mandelic

acid. Dilute nitric acid converts it, first, into benzoyl-formic acid, then into benzoic acid. When heated with hydriodic acid it forms phenyl-acetic acid ; with hydrobromic and hydrochloric acids chloro-phenyl or bromo-phenyl-acetic acids are formed. On the decomposition of mandelic acid by sulphuric acid, see C. 1903, II. 284.

Lævo- and *dextro-mandelic acids* melt at 133°. They have equal, but opposite, molecular rotatory power. Towards reagents they behave like para-mandelic acid. Lævo-mandelic acid, *natural mandelic acid*, results upon digesting amygdalin (*q.v.*) with fuming hydrochloric acid (1848 : Wöhler, A. **66,** 240). Fermentation of ammonium-para-mandelate with *Penicillium glaucum* destroys the lævo-acid, and there remains the dextro-acid. *Schizomyceten* first destroys the dextro-mandelic acid in para-mandelic acid ; the lævo-acid remains (Lewkowitsch, B. **17,** 2723). The direct splitting up of para-mandelic acid into the dextro- and lævo-acids can be brought about by the crystallisation of the cinchonine salt. The mixing together of the dextro- and lævo-acids (molecular quantities) results in the formation of inactive para-mandelic acid. When the dextro- or lævo-acid is heated in a tube to 160° it is converted into the inactive mandelic acid.

A direct transformation of the two active forms into each other is accomplished as follows :—With PCl_5, d-mandelic acid gives l-phenyl-chloracetic acid, and this, with NH_3, gives d-phenyl-alanin, which is converted into l-mandelic acid by means of HNO_2 (Walden's reversal, Vol. I.). The transformation of l-mandelic acid into the dextro-form is done in a similar manner (C. 1909, II. 23).

Derivatives of Para-mandelic Acid.—The **methyl** and **ethyl esters** melt at 52° and 34° (B. **28,** 259). **Amide,** m.p. 131° (B. **25,** 2212). **Hydrazide,** m.p. 132°, gives, with HNO_2, the very unstable azide, which, in contrast with other carboxylic azides, decomposes with alcohol into benzaldehyde, N_2, and allophanic acid ester (B. **34,** 2794). **Methyl-ether acid,** m.p. 71°. **Dimethyl-ether ester,** m.p. 246° (A. **220,** 40). Diethyl-ether ester, see C. 1899, II. 622. **Acetyl-mandelic acid,** m.p. 80°. **Acetyl-mandelic chloride,** b.p.$_{12}$ 132° ; **amide,** m.p. 112° ; **anilide,** m.p. 117·5° ; **ethyl ester,** m.p. 74° (A. **368,** 57).

Mandelic chloralide, m.p. 82° (A. **193,** 40). **Diphenyl-glycolide** $C_6H_5CH\langle{}^{O.CO}_{CO.O}\rangle CHC_6H_5$, m.p. 240°, from mandelic acid in pyridin with phosgene (B. **35,** 3642).

Mandelic acid nitrile $C_6H_5.CHOH.CN$ is a colourless oil, solidifying at −10°. At 170° it breaks down into prussic acid and benzaldehyde. Like mandelic acid, the nitrile is also obtained in a lævo- and a dextro-form, from which, by saponification and reversal, active mandelic acids can be prepared.

On standing with fuming hydrochloric acid it passes into the amide ; and, when heated, into phenyl-chloracetic acid (B. **14,** 1967). It condenses with benzaldehyde in different ways : by the action of alcoholic dilute HCl to $C_6H_5CH[OCH(CN)C_6H_5]_2$, and by the action of etheric · HCl to diphenyl-oxazol and benzylidene-mandelic amide $C_6H_5CH : NCOCH(OH)C_6H_5$ (B. **29,** 207, R. 791 ; **35,** 1590).

Derivatives of mandelic acid are **trichloro-methyl-** and **tribromo-methyl-phenyl-carbinol** $CCl_3CH(OH)C_6H_5$, b.p.$_{25}$ 155°, and $CBr_3CH(OH)C_6H_5$, m.p. 78° ; these compounds are prepared, in a manner

analogous to acetone-chloroform, by combination of benzaldehyde with CCl_3H and CBr_3H, by means of caustic potash, or by the action of C_6H_5MgBr upon chloral; they are convertible into mandelic acid, or, by reduction with zinc dust, into styrol and halogen styrols (C. 1900, II. 326); on boiling with potassium carbonate they decompose into $CHCl_3$ (or $CHBr_3$) and benzaldehyde (C. 1908, I. 1388).

p-Dimethyl-amido-phenyl-trichlor-ethyl alcohol $(CH_3)_2NC_6H_4CH(OH)CCl_3$, from dimethyl-aniline and chloral (B. **19,** 365); **p-dimethyl-amido-mandelic nitrile** $(CH_3)_2N[4]C_6H_4CH(OH)CN$, m.p. 114°, from **p-dimethyl-amido-benzaldehyde** (B. **85,** 3571).

p-Bromo- and **p-Iodo-mandelic acids** melt at 117° and 133° (B. **24,** 997; **23,** 3467). **o-, m-,** and **p-Nitro-mandelic acids** melt at 140°, 119°, and 126° (B. **20,** 2203; **22,** 208). For a peculiar reduction product of the latter, see B. **41,** 373.

o-Amido-mandelic acid, *hydrindic acid* $NH_2[2]C_6H_4CH(OH)CO_2H$, is not stable in a free condition. Its *sodium salt* $C_8H_8NO_3Na+H_2O$ is formed in the reduction of isatin with sodium amalgam. From concentrated solutions of the sodium salt, acids separate.

Dioxindol, *o-amido-mandelic acid lactame* $C_6H_4\begin{cases}[1]CH(OH)CO\\[2]NH\text{——}\end{cases}$. This is also produced when isatin and zinc dust, water, and some hydrochloric acid are boiled.

Acetyl-dioxindol, melting at 127°, is converted by baryta water into **o-acetamido-mandelic acid** $CH_3CONH[2]C_6H_4CH(OH)CO_2H$, melting at 142°, which also results from the reduction of acetyl-isatinic acid. Hydriodic acid or sodium amalgam change it to oxindol (p. 310).

o-Oxy-mandelic acid, obtained from salicyl-aldehyde, prussic acid, and also from o-oxy-phenyl-glyoxylic acid, is a syrupy mass. An optically active oxy-mandelic acid is formed from helicin tetra-acetate with HCN and saponification (C. 1902, II. 214). Its *lactone* melts at 49° and boils at 237° (B. **14,** 1317; **17,** 974). **p-Methoxy-mandelic acid,** from anisaldehyde, melts at 93° (B. **14,** 1976). **2, 5-Dioxy-mandelic acid,** m.p. 143° with decomposition, by reduction of hydroquinone-glyoxylic acid.

Phenyl-chloracetic acid $C_6H_5.CHCl.CO_2H$, melting at 78°, is produced when mandelic acid is heated with concentrated hydrochloric acid to 140°; from trichloro-methyl-phenyl-carbinol with KHO (C. 1897, I. 1014); and by action of water upon its chloride. Its *chloride* $C_6H_5.CHCl.COCl$, formed by the action of PCl_5 upon mandelic acid, boils at 125° (45 mm.) (A. **279,** 122).

Phenyl-bromacetic acid $C_6H_5.CHBrCO_2H$ melts at 83°. Its *ethyl ester,* boiling at 145° (10 mm.) (B. **24,** 1877), when heated with potassium cyanide becomes diphenyl-succinic ester. *Chloride,* $b.p._{18}$ 118°. Its *nitrile,* from benzyl cyanide and bromine, when heated alone becomes stilbene; when heated with potassium cyanide it yields stilbene or dicyano-dibenzyl (*q.v.*); while with alcoholic potash stilbene-dicarboxylic acid or diphenyl-maleïc acid is produced.

Phenyl-nitro-acetic ester and **phenyl-nitro-aceto-nitrile** are formed as sodium salts $C_6H_5C(NOONa)CO_2C_2H_5$ and $C_6H_5C(NOONa)CN$ from phenyl-acetic ester and benzyl cyanide, with ethyl nitrate and sodium alcoholate; the free acids are very unstable; saponification with NaHO yields sodium-phenyl-nitro-methane; and reduction of sodium-phenyl-

nitro-aceto-nitrile, with zinc dust, yields **iso-nitroso-benzyl cyanide** $C_6H_5C(NOH)CN$ (B. **35,** 1755 ; **42,** 1930).

Phenyl-amido-acetic acid $C_6H_5.CH(NH_2).CO_2H$ melts at 256°. It yields CO_2 and benzyl-amine when it is distilled. It results (1) on treating phenyl-bromo-acetic acid with aqueous ammonia (B. **11,** 2002) ; (2) on boiling its nitrile with dilute sulphuric acid (B. **18,** 383) ; and (3) by the reduction of its oxime or the phenyl-hydrazone of benzoyl-formic acid (A. **227,** 344).

By means of d-camphor-sulphonic acid, or by decomposition of the formyl compound, m.p. 180°, with cinchonin or quinine, phenyl-amido-acetic acid has been split up into its optically active components with coefficient 157·8°. The l-acid is also formed on partial fermentation of the racemic acid with yeast (B. **41,** 1286, 2071). Its *methyl ester* melts at 32°. *Cyclic double-acid amide* $C_6H_5.CH\langle{}^{CO—NH}_{NH—CO}\rangle CH.C_6H_5$ melts with decomposition at 274° (B. **24,** 4149). Its *nitrile* is a yellow oil, which gradually solidifies to a crystalline mass. It is very decomposable. It results from the action of ammonia upon mandelic nitrile.

Alkylic and phenylated phenyl-amido-acetic acids are obtained as the result of the action of methyl-amine, aniline, and similar bases upon phenyl-bromo-acetic acid (B. **15,** 2031). Starting from phenyl-bromo-acetic chloride, a number of di- and poly-peptides, like phenyl-glycyl-glycin, phenyl-glycyl-alanin, etc., have been prepared (A. **340,** 190).

α-Anilido-phenyl-acetic nitrile $C_6H_5CH(NHC_6H_5)CN$, m.p. 85°, is easily obtained from benzylidene-aniline and prussic acid, as well as from mandelic acid nitrile with aniline ; on boiling with alcoholic potash, it combines with benzaldehyde to form the *benzylidene* compound of the corresponding acid amide :

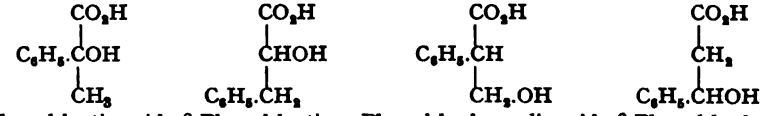
$$C_6H_5CH(NHC_6H_5)CN+C_6H_5CHO=C_6H_5CH(NHC_6H_5)CON : CHC_6H_5.$$

The latter substance is very stable, and is also formed by the action of KCN upon a mixture of benzylidene-aniline and benzaldehyde (B. **31,** 2699). **p-Dimethyl-amido-phenyl-anilido-aceto-nitrile** $(CH_3)_2NC_6H_4CH(NHC_6H_5)CN$, m.p. 114° (B. **35,** 3572).

Urethano-phenyl-aceto-nitrile $C_6H_5CH(NHCO_2C_2H_5)CN$, m.p. 83°, from mandelic acid nitrile with urethane and zinc chloride (B. **34,** 370).

Of the alphyl-glycollic acids, mention may yet be made of **p-isopropyl-mandelic acid,** prepared from cumic aldehyde, prussic acid, and hydrochloric acid. It, too, has been resolved by means of quinine into its active isomerides (B. **26,** R. 89).

Phenyl-oxy-propionic Acids, Phenyl-lactic Acids.—There are four possible structural isomerides. All are known, and contain an asymmetric carbon atom :



α-Phenyl-lactic acid, atro-lactinic acid

β-Phenyl-lactic acid

α-Phenyl-hydracrylic acid, tropaic acid

β-Phenyl-hydracrylic acid.

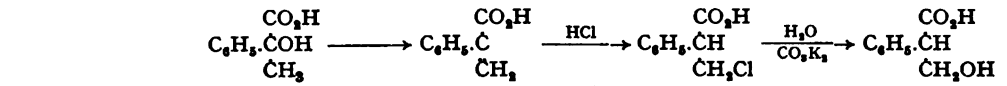
1. **Atro-lactinic acid,** *α-phenyl-lactic acid* $C_9H_{10}O_3+1\frac{1}{2}H_2O$, melts when in the hydrous state at 90°, and when anhydrous at 94°. It is

obtained from α-bromo-hydro-atropic acid when the latter is boiled with a soda solution, from hydratropic acid with $KMnO_4$, from its nitrile, the addition product of prussic acid on aceto-phenone, by boiling with dilute HCl (B. **14,** 1980); its ethyl ester, b.p. 259°, is also formed from phenyl-glyoxylic ester with methyl-magnesium iodide. When boiled with concentrated hydrochloric acid it decomposes into water and atropic acid.

Corresponding to atro-lactinic acid are **α-chloro-** and **α-bromo-hydratropic acids,** melting at 73° and 93°, which are produced when it stands in contact with concentrated haloid acids (A. **209,** 3). **α-Amido-hydratropic acid** sublimes, without melting, at 260° (B. **14,** 1981).

2. **Tropic acid,** *α-phenyl-hydracrylic acid,* is known in an inactive, decomposable, and two optically active modifications.

Inactive tropic acid, melting at 117°, is obtained, together with tropine (*q.v.*) (A. **138,** 233; B. **13,** 254), on digesting (60°) the alkaloids atropine and hyoscyamine with baryta water. It was made synthetically from atropic acid, the decomposition product of atro-lactinic acid, by changing it with concentrated hydrochloric acid into β-chloro-hydratropic acid, which boiling potassium carbonate converts into inactive tropic acid:



Lævo- and **dextro-tropic acids,** melting at 128° and 123°, can be separated by the fractional crystallisation of their quinine salts, and are thus prepared from r-tropic acid. The dextro-quinine salt, more sparingly soluble in dilute alcohol, melts at 186°, and the lævo-salt at 178° (B. **22,** 2591).

β-Chloro- and **β-bromo-hydratropic acids** melt at 87° and 93°.

β-Amido-hydratropic acid melts at 119° (A. **209,** 3).

3. **β-Phenyl-lactic acid, benzyl-glycollic acid** $C_6H_5.CH_2.CH.(OH).CO_2H$, melting at 97°, is derived from phenyl-acetaldehyde, with prussic acid and hydrochloric acid, and from benzyl-tartronic acid upon heating it to 180°. Heated with dilute sulphuric acid, it decomposes into phenyl-acetaldehyde and formic acid.

α-Bromo-hydro-cinnamic acid $C_6H_5CH_2.CHBr.COOH$, m.p. 49°, is formed from benzyl-malonic acid by bromination and CO_2 elimination. Chloride, b.p.$_{12}$ 133° (B. **39,** 3999).

Phenyl-alanin, *β-phenyl-α-amido-propionic acid* $C_6H_5.CH_2.CH(NH_2).CO_2H$ sublimes without decomposition when it is slowly heated. Upon rapid heating it yields phenyl-ethyl-amine and a *cyclic double-acid amide* $C_6H_5.CH_2.CH.\langle\begin{matrix}CO.NH\\NH.CO\end{matrix}\rangle CH.CH_2.C_6H_5$, m.p. 290° (A. **219,** 188; **271,** 169). It is found along with asparagin in the sprouts of *'Lupinus luteus,* and is formed in the decay, or by the chemical decomposition, of albumen, caseïn, or gelatin, and can be separated out from mixtures by means of its sparsely soluble phospho-tungstate compound (C. 1902, II. 272). Synthetically, the optically inactive form is prepared from its nitrile, the product of the action of ammonia upon the nitrile of β-phenyl-lactic acid, with hydrochloric acid; further,

by the reduction of α-amido-cinnamic acid (B. **17,** 1623), and of α-isonitroso-β-phenyl-propionic acid (A. **271,** 169). Also from phthalimido-benzyl-malonic ester $C_6H_4(CO)_2NC(CH_2C_6H_5)(COOR)_2$ by splitting (C. 1903, II. 33) and by the action of NH_3 upon α-bromo-hydrocinnamic acid. From the inactive phenyl-alanin thus obtained, the d- and l-bodies of rotation coefficient ±35° are obtained by partial fermentation with yeast, or by breaking up the formyl compound with brucin (A. **357,** 2 ; C. 1908, I. 1632).

Benzoyl-phenyl-alanin, from benzoyl-amido-cinnamic acid by reduction, melts at 182° (A. **275,** 15).

Phenacetyl-phenyl-alanin $C_6H_5CH_2CH(NHCOCH_2C_6H_5)COOH$, m.p. 126°, is obtained in the same way ; and also by a peculiar reaction of ammonia with phenyl-pyro-racemic acid (A. **307,** 146). Phenyl-alanin-ethyl ester, b.p.$_{10}$ 143° (C. 1901, I. 679).

A considerable number of di- and polypeptides containing the phenyl-alanin complex, like phenyl-alanyl-glycin, phenyl-alanyl-phenyl-alanin, and leucyl-glycyl-phenyl-alanin, have been obtained by the methods described in Vol. I., starting from active and inactive phenyl-alanin or from α-bromo-hydro-cinnamic chloride (A. **354,** 1 ; **357,** 1).

o- and **p-Nitro-phenyl-lactic acids** are produced in the nitration of phenyl-lactic acid. When reduced the o-acid yields **oxy-hydro-carbo-styril** $C_6H_4\begin{cases}[1]CH_2—CH.OH \\ [2]NH—CO\end{cases}$, m.p. 197°, and the p-acid, **p-amido-β-phenyl-lactic acid** $NH_2[4]C_6H_4.CH_2.CH(OH)CO_2H$, melting with decomposition at 188°.

o-Oxy-phenyl-lactic acid, *salicyl-lactic acid* $HO[2]C_6H_4CH_2CH(OH)CO_2H$, is a syrup-like mass. It results from the action of sodium amalgam upon o-oxy-phenyl-pyro-racemic acid (B. **18,** 1188). Its inner phenol-alcohol anhydride is **hydro-cumarilic acid** $C_6H_4\begin{cases}[1]CH_2.CH.CO_2H \\ [2]O——\end{cases}$, melting at 118°. This is the reduction product of cumarilic acid (A. **216,** 166). **p-Oxy-phenyl-lactic acid** melts at 144° in the anhydrous condition. It is formed when an excess of nitrous acid acts upon p-amido-phenyl-alanin (A. **219,** 226).

2, 4-Dioxy-phenyl-lactic acid, *hydroquinone lactic acid,* m.p. 87°, see C. 1907, II. 901. **p-Iodo-phenyl-alanin,** m.p. 270° with decomposition (see C. 1909, I. 70 ; B. **42,** 3411).

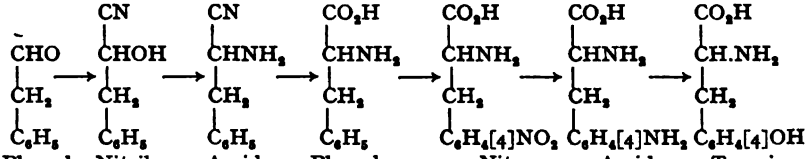
p-Nitro-phenyl-alanin $NO_2[4]C_6H_4CH_2.CH(NH_2)CO_2H$ decomposes at 240°. It is formed in the nitration of phenyl-alanin.

p-Amido-phenyl-alanin $NH_2[4]C_6H_4.CH_2.CH(NH_2).CO_2H$ is produced in the reduction of p-nitro-phenyl-alanin and p-nitro-phenyl-α-nitro-acrylic acid.

Tyrosin, *p-oxy-phenyl-alanin* $HO[4]C_6H_4.CH_2CH(NH_2)CO_2H$, melts at 235°. It occurs in the liver when its functions are disturbed, the spleen, the pancreas, and in stale cheese (τυρός), and is formed from animal substances (urea, horn, hair, albumen) on boiling them with hydrochloric or sulphuric acid ; by fusion with alkalies or by putrefaction (together with leucine, aspartic acid, etc.). It may be prepared synthetically from p-amido-phenyl-alanin by the action of one molecule of potassium nitrite upon the hydrochloric acid salt, or by splitting up synthetic benzoyl-tyrosin.

History.—Liebig discovered tyrosin upon fusing freshly prepared cheese with caustic potash (1846) (A. **57,** 127; **62,** 269). E. Erlenmeyer, sen., and Lipp (A. **219,** 161) succeeded in synthesising tyrosin, beginning with phenyl-acetaldehyde.

Synthesis of Tyrosin.—Phenyl-acetaldehyde and prussic acid yield the nitrile of phenyl-lactic acid. Ammonia changes the latter to the nitrile of phenyl-alanin, which hydrochloric acid converts into phenyl-alanin. The latter by nitration yields p-nitro-phenyl-alanin, whose reduction product, *p-amido-phenyl-alanin hydrochloride,* is changed by an equimolecular quantity of nitrous acid into *tyrosin* :



A more convenient method has recently been found by E. Erlenmeyer, jun. (see A. **307,** 138; B. **32,** 3638).

Properties and Behaviour.—It dissolves in 150 parts of boiling water, and crystallises in delicate, silky needles. It dissolves in alcohol with difficulty, and is insoluble in ether.

Mercuric nitrate produces a yellow precipitate, which becomes dark red in colour if it be boiled with fuming nitric acid to which considerable water has been added (delicate reaction). Being an amido-acid, tyrosin unites with acids and bases, forming salts. If it be heated to 270° it decomposes into carbon dioxide and oxy-phenyl-ethyl-amine $C_6H_4(OH).CH_2.CH_2.NH_2$. When fused with caustic potash it yields para-oxy-benzoic acid, ammonia, and acetic acid. Putrefaction causes the formation of hydro-para-cumaric acid, and nitrous acid converts the tyrosin into para-oxy-phenyl-lactic acid (A. **219,** 226). Many di- and polypeptides have been formed by the combination of active and inactive tyrosin with other amido-acids (B. **41,** 2840, 2860). By analytical methods also, such as the hydrolysis of silk fibroïn with HCl, a dipeptide containing the tyrosin complex, glycyl-tyrosin, as well as a tetrapeptide, have been isolated (B. **40,** 3544).

Very noteworthy is the natural occurrence of **inactive 3, 5-di-iodo-tyrosin** $OH[4]I_2[3, 5]C_6H_2CH_2.CH(NH_2).CO_2H$, m.p. 213°, first extracted from the coral *Gorgonia Carolinii* (C. 1896, I. 864), and hence called *iodogorgic acid.* Synthetically, it has been prepared by iodination of tyrosin in alkaline solution (C. 1905, I. 1388). On polypeptides with 3, 5-di-iodo-l-tyrosin, see B. **41,** 1237.

4. **β-Phenyl-hydracrylic acid** $C_6H_5.CH(OH).CH_2.CO_2H$, commonly called *phenyl-lactic acid,* results on boiling β-bromo-hydro-cinnamic acid with water (A. **195,** 138), and in the reduction of benzoyl-acetic ester, as well as by the addition of hypochlorous acid to cinnamic acid, and then reducing the resulting chloro-acid with sodium amalgam. The acid melts at 93°. When heated with dilute sulphuric acid it decomposes (like the aliphatic β-oxy-acids) at 190° into water and cinnamic

acid (together with a little styrol) (B. **13,** 304). When digested with concentrated haloid acids it forms β-halogen-hydro-cinnamic acids (*q.v.*). α- and β-Alkylated β-phenyl-hydracrylic acids have been obtained by the action of α-bromo-aliphatic acid esters, and zinc, upon benzaldehyde and aromatic α-ketones.

α-Methyl-β-phenyl-ethylene - lactic acid $C_6H_5CH(OH)CH(CH_3)COOH$, m.p. 95°. **α-Dimethyl-β, p-tolyl-ethylene-lactic acid,** m.p. 112°. **α-Iso-propyl-phenyl-ethylene-lactic acid,** m.p. 107° (C. 1898, I. 668, 884; 1900, II. 533; 1902, I. 1293; 1903, II. 566; B. **40,** 1589; **41,** 5).

o-, m-, and **p-Nitro-phenyl-lactic acids,** or *-hydracrylic acids* $NO_2.C_6H_4CH(OH).CH_2.CO_2H$, melt at 126°, 105°, and 132°. The three isomerides result upon treating the three nitro-β-bromo-hydro-cinnamic acids with sodium carbonate, when (in the cold) the **o-, m-,** and **p-nitro-phenyl-lactic acid lactones,** $NO_2C_6H_4\overset{O\text{—}CO}{\underset{}{CH}}.\underset{}{CH_2}$, melting at 124°, 98°, and 92°, are also produced. *These are the only β-lactones known* (B. **17,** 595, 1659).

The ortho-nitro-acid results, further, by oxidising the aldehyde first produced with silver oxide (B. **16,** 2206). When heated to 190° with dilute sulphuric acid it yields o-nitro-cinnamic acid. Its lactone decomposes on boiling with water into carbon dioxide and o-nitro-styrol; it yields β-oxy-hydro-carbo-styrol when reduced.

β-Chloro-, bromo-, and **Iodo-hydro-cinnamic acids** $C_6H_5.CHX.CH_2.CO_2H$ melt at 126°, 137°, and 120°. They are obtained from cinnamic acid or β-phenyl-acrylic acid by the addition of halogen hydrides in aqueous or glacial acetic acid solution (B. **11,** 1211) and from β-phenyl-hydracrylic acid (*q.v.*). When heated or boiled with water the free acids decompose, with previous formation of β-oxy-acids, into halogen hydride and cinnamic acid. When neutralised, even in the cold, with alkali carbonates they break down into haloid acid, carbon dioxide, and styrol $C_6H_5.CH : CH_2$.

o-, m-, and **p-Nitro-β-bromo-hydro-cinnamic acids** $NO_2C_6H_4CHBr.CH_2.CO_2H$ are produced by the addition of hydrogen bromide, in glacial acetic acid, to the three nitro-cinnamic acids (B. **17,** 596, 1494) (see also Nitro-phenyl-lactic acid lactone).

β-Hydroxylamino-hydro-cinnamic acid $C_6H_5CH(NHOH).CH_2COOH$, m.p. 166° with decomposition, is formed by the attachment of free hydroxylamine to cinnamic acid. By oxidation with ammoniacal silver solution it becomes **γ-phenyl-isoxazolone** (*q.v.*), and with HNO_2 it becomes **N-oxy-γ-phenyl-isoxazolidone** (B. **39,** 3115). On reduction it forms:

β-Amido-hydro-cinnamic acid $C_6H_5.CH(NH_2)CH_2.CO_2H$ melts at 131°, which with HNO_2 yields β-phenyl-hydracrylic acid (B. **38,** 2316).

γ-Phenyl-α-amido-butyric acid $C_6H_5CH_2.CH_2CH(NH_2)COOH$, m.p. 295°, by reduction of benzyl-pyro-racemic acid oxime (B. **39,** 1478).

γ- and δ-Oxy-acids.—*γ-Oxy-acids,* beginning with the phenyl-oxy-butyric acids, are known. They pass readily into their lactones. **γ-Phenyl-γ-oxy-butyric acid** $C_6H_5CH(OH).CH_2.CH_2.CO_2H$ melts at 75°, and slowly decomposes, even at 65°–70°, into water and its lactone, **phenyl-butyro-lactone** $C_{10}H_{10}O_2$. The latter melts at 37° and boils at 306°.

It is obtained from β-benzoyl-propionic acid (B. **15,** 889) and from

phenyl-bromo-butyric acid. Its lactone is formed on boiling phenyl-iso-crotonic acid and phenyl-paraconic acid with dilute sulphuric acid (A. **228,** 178; B. **29,** R. 14; **33,** 3519).

On the relations of **m-tolyl-butyro-lactone** $CH_3C_6H_4\dot{C}HCH_2CH_2C\dot{O}\dot{O}$ towards **cannabinol,** the poisonous resin of Indian hemp, *Cannabis indica,* see C. 1899, I. 118.

α-Phenyl-γ-oxy-valeric acid, only stable in the form of liquid lactone (B. **17,** 73).

γ-Phenyl-γ-valero-lactone, b.p.$_{16}$ 169° (C. 1902, II. 1359).

δ-Benzyl-γ-oxy-valeric acid melts at 101°, and its **lactone** at 33° (A. **268,** 94).

β-Benzyl-γ-oxy-valeric acid melts at 75°, and its lactone at 86° (A. **254,** 215). It is obtained from benzal-lævulinic acid.

α-Benzyl-δ-oxy-valeric acid (B. **24,** 2447).

B. **Dioxy-alcohol Acids** are chiefly obtained by oxidising the phenyl-olefin-carboxylic acids with potassium permanganate (A. **268,** 44; **283,** 338). The two possible phenyl-glyceric acids are known.

Atro-glyceric acid, α-phenyl-glyceric acid $CH_2OH.C(C_6H_5)OH.CO_2H$, melting at 146°, results on boiling α, β-dibromo-hydratropic acid with excess of alkalies, and, from benzoyl-carbinol, by means of prussic acid and hydrochloric acid (B. **16,** 1292). It breaks down into CO_2 and phenyl-acetaldehyde upon heating.

Dibromo-hydratropic acid $CH_2Br.C(C_6H_5)Br.CO_2H$, melting at 115°, is produced when bromine acts upon atropic acid. It decomposes on boiling with water into aceto-phenone, CO_2, and HBr.

Styceric acid, β-phenyl-glyceric acid $C_6H_5.CHOH.CHOH.COOH$, contains two unsym. carbon atoms, and therefore occurs in different modifications. An acid of m.p. 121° is obtained by saponification with alcoholic potash from its dibenzoyl-ethyl ester $C_6H_5CH(OCOC_6H_5)CH(OCOC_6H_5)COOC_2H_5$, m.p. 109°, the result of the action of silver benzoate upon cinnamic ester dibromide; on saponifying the dibenzoyl ester with aqueous alkaline hydroxide an acid is formed, melting at 141° with decomposition, which is also obtained by the oxidation of cinnamic acid with $KMnO_4$. It dissolves in ether with difficulty, and yields on the gradual benzoylation of its ethyl ester a dibenzoyl ester of m.p. 85°, while benzoylation at a higher temperature produces transposition into an ester of m.p. 109°. The m.p. 121° acid is racemic, and may be split up into two optical antipodes by means of the stycerin salt, a- and l-styceric acid, m.p. 167°, $\alpha_D = +31{\cdot}08°$ and $-30{\cdot}23°$ respectively, while the m.p. 141° acid has not hitherto been so split up (B. **30,** 1600). It is significant that oxidation of the ordinary fumaroid cinnamic acid with $KMnO_4$ yields the m.p. 141° acid, while the maleïnoid allo-cinnamic acid yields the m.p. 121° acid (B. **41,** 2411). On heating above their melting-points, the acids break up into CO_2 and phenyl-acetaldehyde. On warming with H_2SO_4, concentrated HCl, or acetic anhydride water, is split off and phenyl-pyro-racemic acid formed (B. **43,** 1032). With HBr the m.p. 121° acid gives a **phenyl-β-bromo-α-oxy-propionic acid** of m.p. 157°, while the other gives a bromoxy-acid of m.p. 165°.

Benzal-phenyl-glyceric ester $C_6H_5\dot{C}H\!\!<\!\!\begin{matrix}O.CH(C_6H_5).O\\ \text{———}\\ \dot{C}H.CO_2C_2H_5\end{matrix}$ is produced

in two stereo-isomeric forms, melting at 104° and 61° respectively, by the action of diazo-acetic ester upon benzaldehyde. The benzal-phenyl-glyceric acids, m.p. 132° and 156° respectively, are split up by acetic acid into benzaldehyde and the phenyl-glyceric acids, m.p. 121° and 141°. The latter, on shaking up with benzaldehyde and 50 per cent. H_2SO_4, regenerates the benzal-phenyl-glyceric acid, m.p. 156° (B. **48,** 1024).

p-Nitro-phenyl-glyceric acid, melting at 167°, is obtained from p-nitro-phenyl-glycidic acid.

o-Amido-phenyl-glyceric acid, m.p. 218°.

Phenyl-α-chloro-β-lactic acid $C_6H_5.CH(OH)CH.Cl.CO_2H+H_2O$ melts at 56°, and, when anhydrous, at 86°. It results from the action of hypochlorous acid upon cinnamic acid. Sodium amalgam reduces it to phenyl-lactic acid, alkalies change it to phenyl-glycidic acid and phenyl-glyceric acid, while, with fuming hydrochloric acid, it yields phenyl-dichloro-propionic acid (B. **22,** 3140).

Phenyl-α-bromo-β-lactic acid $C_6H_5.CH(OH).CHBr.CO_2H+H_2O$ melts at 125° when anhydrous. It is formed on boiling phenyl-dibromo-propionic acid with water (B. **13,** 310). It has been separated, by means of cinchonin, into two optically active components (B. **24,** 2831; **32,** 2375).

Phenyl-α-iodo-β-lactic acid $C_6H_5.CH(OH).CHI.CO_2H$ melts at 137° with decomposition. It results from the action of an aqueous chloro-iodine solution upon cinnamic acid (B. **19,** 2464). **o-** and **p-Nitro-phenyl-α-chloro-lactic acids** melt at 119° and 165°. The o- body is converted by sodium amalgam into indol (B. **13,** 2261; **19,** 2646).

β-Phenyl-α-amido-hydracrylic acid, *phenyl-serin* $C_6H_5.CH.(OH).CH(NH_2).CO_2H+H_2O$, decomposing at 194°, is formed from its benzylidene compound, the condensation product of benzaldehyde and glycocoll, obtained with NaHO and acids, besides a more soluble stereo-isomeric acid (A. **307,** 84).

The isomeric **β-phenyl-β-amido-lactic acid,** *phenyl-iso-serin* $C_6H_5 CH(NH_2).CH(OH).CO_2H$, m.p. 241° with decomposition, is obtained by the attachment of NH_3 to sodium in the cold (B. **39,** 791).

β-Phenyl-β-chloro-α-oxy-propionic acid $C_6H_5.CHCl.CH(OH).CO_2H$, m.p. 141°, and **phenyl-β-bromo-α-oxy-propionic acid** are obtained from phenyl-glyceric acid with fuming halogen hydrates (B. **16,** 1290).

o- and **p-Nitro-phenyl-β-chloro-lactic acids,** melting at 125° and 167°, are obtained by the action of fuming hydrochloric acid upon the corresponding glycidic acids (B. **19,** 2646).

o-Nitro-phenyl-β-bromo-lactic acid melts at 135° (B. **17,** 221).

Cinnamic acid dichloride, *α, β-dichloro-hydro-cinnamic acid* $C_6H_5.CHCl.CHCl.CO_2H$, melting at 163°, results when chlorine acts upon cinnamic acid in carbon disulphide solution and on treating phenyl-α-chloro-lactic acid with fuming hydrochloric acid (B. **14,** 1867).

Allo-cinnamic acid dichloride is an oil decomposable by strychnine into two optically active components (B. **27,** 2041).

Cinnamic acid dibromide, *α, β-dibromo-hydro-cinnamic acid,* melting at 195°, yields CO_2, phenyl-acetaldehyde, cinnamic acid, and phenyl-α-bromo-lactic acid on boiling with water. Strychnine resolves it into two optically active components (B. **26,** 1664). The *methyl ester* melts at 117°. The *ethyl ester* melts at 69° (B. **22,** 1181; C. 1903, II. 115).

Allo-cinnamic acid dibromide melts at 91°–93°. It is separated into two optically active components by cinchonin (B. **27,** 2039). The *methyl ester* melts at 52°–53°.

o- and **p-Nitro-α, β-dibromo-hydro-cinnamic acids** melt at 180° and 227°. The o- and *p-ethyl esters* melt at 71° and 110° (A. **212,** 151).

o-Methoxy-cinnamic acid dibromide, m.p. 170°; **piperonyl acid dibromide,** m.p. 156°. In these dibromides the Br atom adjoining the phenyl nucleus is very reactive (B. **39,** 27; **40,** 2174).

Phenyl-glycidic acid $C_6H_5.CH\overset{O}{\diagdown\diagup}CH.CO_2H$, separated from the sodium salt, is an oil solidifying at 0°. It results from the action of alkalies upon α- and β-chloro-phenyl-lactic acids, as well as by the condensation of benzaldehyde with chloracetic ester (A. **271,** 137). Phenyl-glycidic acid is very unstable. It readily decomposes into CO_2 and phenyl-acetaldehyde. On boiling with water phenyl-glyceric acid is also produced. Hot concentrated HCl partly converts phenyl-glycidic acid into the isomeric phenyl-pyro-racemic acid (B. **33,** 3001). From the optically active phenyl-α-bromo-lactic acids the optically active phenyl-glycidic acids are obtained in the form of their sodium salts.

Numerous homologous phenyl-glycidic esters have been obtained by condensation of aromatic aldehydes and ketones with chloracetic ester, or chloro-propionic ester, by means of Na ethylate or amide (C. 1905, I. 346; 1906, I. 669; B. **38,** 699). The free acids obtained by saponification, like the phenyl-glycidic acid itself, easily splits up into CO_2 and aldehydes or ketones. **β-Methyl-** and **ethyl-phenyl-glycidic ethyl ester,** b.p. 148° and 149°. **α-Methyl-phenyl-glycidic ethyl ester,** b.p.$_{18}$ 153°.

o-Nitro-phenyl-glycidic acid $NO_2[2]C_6H_4CH\overset{O}{\diagdown\diagup}CH.CO_2H + H_2O$ melts at 94°, and at 125° when anhydrous. It is produced when alcoholic potash acts upon o-nitro-phenyl-lactic acid, or by the action of sodium hypochlorite upon o-nitro-phenyl-lactic acid ketone (A. **284,** 135). It breaks down, on heating, into CO_2 and *indigo*. It yields anthranile and anthroxan-aldehyde on boiling with water (B. **19,** 2649).

Phenyl-α-oxy-butyro-lactone $C_6H_5\overset{\vert_____\vert}{CH}.CH_2.CH(OH)\overset{\vert}{CO}\overset{\vert}{O}$, m.p. 125°, from benzoyl-pyro-racemic acid by reduction with Na amalgam, is transformed into β-benzoyl-propionic acid by boiling with dilute HCl (B. **35,** 3767).

C. **Trioxy-alcohol Acids.**—*γ-Phenyl-trioxy-butyric acid* $C_6H_5[CH.OH]_3CO_2H$ passes readily into the *lactone*, melting at 115°–117°; by reduction this yields phenyl-tetrose. γ-Phenyl-trioxy-butyric acid is prepared by starting with the dibromide of cinnamic aldehyde cyanhydrin (B. **25,** 2556; A. **319,** 206).

(7) Phenyl-paraffin-aldehyde-carboxylic Acids.

As explained under the aliphatic unsaturated ketols, oxy-olefin-carboxylic acids and oxy-ketone-carboxylic acids, the oxy-methylene derivatives are produced by the condensation of acetone, acetic ester, acèto-acetic ester, and other bodies with formic ester in the presence of sodium ethylate. As these compounds conduct themselves in many respects like aldehydes, it was originally supposed that they contained

the aldehyde group, and it was only their very pronounced acid character which led to considering them as *oxy-methylene* compounds. It is rather remarkable that two isomeric esters are formed in the condensation of phenyl-acetic ester and formic ester by means of sodium ethylate. Both bodies yield the same derivatives with phenyl-hydrazin. The one is a liquid and the other a solid.

Both forms, especially when dissolved, can quite easily be converted into each other. The liquid form is that of the metallic compounds, and is distinguished from the solid form by the strong blue-violet colour produced by ferric chloride. It also reacts more easily with phenyl cyanate. It is assumed that the liquid form corresponds to the *enol* form of formyl-phenyl-acetic ester, and the solid form to the *aldo* form of the same (W. Wislicenus, A. **312,** 34 ; also B. **39,** 203).

Oxy-methylene-phenyl-acetic ethyl ester $CH(OH) : C(C_6H_5)CO_2C_2H_5$ is a liquid boiling at 144° (16 mm.). Ferric chloride imparts a violet colour to it. Its sodium compound gives, with benzoyl chloride, a liquid, unstable α-benzoate $CH(OCOC_6H_5) : CH(C_6H_5)CO_2C_2H_5$, which is converted, on distillation, into a geometrically isomeric stable β-benzoate, m.p. 88°. Methyl ester, m.p. 41°.

Phenyl-formyl-acetic ethyl ester $CHO.CH(C_6H_5)CO_2C_2H_5$ melts at 70°, passing at the same time into the liquid isomeric ester. Methyl ester, m.p. 73° (C. 1900, I. 122).

(8) Phenyl-paraffin-ketone-carboxylic Acids.

The acids belonging to this group can be arranged, like the aliphatic ketone-carboxylic acids, as α-, β-, and γ-ketone-carboxylic acids, and in each of these groups we can have sub-groups, depending upon whether the ketone group is in direct union with the benzene nucleus or not.

A. **α-Ketone-carboxylic Acids** result from the oxidation (1) of ketones ; (2) of glycols ; (3) of ketone alcohols ; (4) of alcohol-carboxylic acids ; (5) (nuclear synthetic) from cyanides of the acid radicles by saponification with cold concentrated hydrochloric acid ; (6) from benzenes by the action of chloroxalic esters in the presence of aluminium chloride (B. **20,** 2045 ; C. 1898, I. 26, 42).

Phenyl-glyoxylic acid, *benzoyl-formic acid* $C_6H_5.CO.CO_2H$, melting at 65°, and isomeric with the phthal-aldehydic acids, is obtained by oxidising aceto-phenone with potassium ferricyanide (B. **20,** 389), as well as by oxidising phenyl-glycol, benzoyl-carbinol, and mandelic acid with nitric acid :

$$\left.\begin{matrix} C_6H_5CO.CH_3 \\ C_6H_5CH(OH).CH_2OH \end{matrix}\right\rangle \longrightarrow C_6H_5COCOOH \longleftarrow \left\langle\begin{matrix} C_6H_5CO.CH_2OH \\ C_6H_5CH(OH)CO_2H \end{matrix}\right.$$

The acid was first prepared (by nuclear synthesis) by saponifying benzoyl cyanide, its nitrile, obtained from benzoyl chloride and mercury, or silver cyanide (Claisen). Its ethyl ester is formed when ethyl-chloroxalic ester acts upon mercury diphenyl or upon benzene in the presence of $AlCl_3$.

The acid is very soluble in water, and, when distilled, decomposes into CO and benzoic acid, with a small division into CO_2 and benzaldehyde. Heating with aniline splits it up into CO_2 and benzylidene-aniline, a reaction useful for forming aldehydes. When mixed with benzene containing thio-phene and sulphuric acid it is coloured deep

red, afterwards blue-violet; all its derivatives, and also isatin, react similarly.

Being a ketonic acid, it unites with sodium bisulphite and with CNH (see Phenyl-tartronic acid). Sodium amalgam converts it into mandelic acid, and hydriodic acid into phenyl-acetic acid. H_2S and the alkali produce thio-phenyl-acetic acid (C. 1903, II. 1271).

Its **methyl ester** boils at 247°. Its **ethyl ester** boils at 257°. The **α-amide** melts at 90°. The **β-amide hydrate** $C_6H_5.CO.CONH_2+H_2O$ melts at 64°. The **γ-amide** melts at 134° (B. **12,** 633; **20,** 397). The **anilide,** from γ-benzil-monoxime (*q.v.*) and PCl_5, melts at 63°.

Benzoyl cyanide $C_6H_5.CO.CN$, melting at 32° and boiling at 207°, is obtained in the distillation of benzoyl chloride with mercuric cyanide, and by the action of acetyl chloride (B. **20,** 2196) upon iso-nitroso-aceto-phenone. Sodium, in absolute alcohol, converts it into **poly-benzoyl cyanide** $(C_8H_5NO_2)x$, melting at 95° (*J. pr. Ch.* 2, **39,** 260). Alkalies change benzoyl cyanide to benzoic acid and potassium cyanide, while concentrated hydrochloric acid converts it into benzoyl-formic acid.

Concerning a trimolecular benzoyl cyanide $(C_8H_5NO)_3$, yellow needles, m.p. 194°, obtained by transforming benzoyl bromide with silver cyanide, see B. **40,** 1655.

Chloro-iso-nitroso-aceto-phenone, *benzoyl-formoximic acid chloride* $C_6H_5.CO.C(:NOH)Cl$, melting at 131°, is produced in the chlorination of iso-nitroso-aceto-phenone (B. **26,** R. 313).

Formazyl-phenyl-ketone $C_6H_5COC(N:NC_6H_5):NNHC_6H_5$, m.p. 142°, from benzoyl-acetic acid or benzoyl-acetone with diazo-benzol, is split by reduction into aniline and **benzoyl-amidrazone** $C_6H_5CO(NH_2):NNHC_6H_5$, m.p. 152° (*J. pr. Ch.* 2, **65,** 139).

Benzoyl cyanide anile $C_6H_5C(:NC_6H_5)CN$, m.p. 72°, from phenyl-anilido-aceto-nitrile by oxidation with permanganate in acetone. Similarly we obtain **p-dimethyl-amido-benzoyl cyanide anile,** m.p. 121° (B. **35,** 3569).

Phenyl-hydrazi-methylene-carboxylic acid $C_6H_5.C(\langle^{NH}_{NH}\rangle).CO_2H$. The hydrazin salt melts at 119°. **Diphenyl-glyoxylic acid hydrazone** $\begin{matrix}C_6H_5.C(:N)CO_2H\\ |\\ C_6H_5.C(:N)CO_2H\end{matrix}$. Its diethyl ester melts at 138° (*J. pr. Ch.* 2, **44,** 567).

Phenyl-glyoxylic acid phenyl-hydrazone melts at 153° (A. **227,** 341).

(β-), **Syn-phenyl-glyoxylic acid oxime** melts at 147°. (α-), **Anti-phenyl-glyoxylic acid oxime, iso-nitroso-phenyl-acetic acid** $C_6H_5.C(:NOH)CO_2H$ melts at 128° (B. **24,** 42). The *methyl ester* melts at 138°. The *dimethyl ester* melts at 56° (B. **16,** 519). **Benzoyl cyanide oxime** $C_6H_5.C(:NOH)CN$, melting at 129° (B. **24,** 3504), is obtained from benzyl cyanide by means of amyl nitrite and sodium or nitrous acid and sodium ethylate. Also from phenyl-glyoxime by boiling with NaHO, or, direct, from ω-dibromo-aceto-phenone with hydroxyl-amine and alkali (B. **24,** 3504; *J. pr. Ch.* 2, **66,** 353).

Substituted Benzoyl-formic Acids.—**o-** and **p-Bromo-benzoyl-formic acids** melt at 93°–103° and 108° (B. **25,** 3298, and **28,** 259).

o-Nitro-benzoyl-formic acid $NO_2.C_6H_4CO.CO_2H+H_2O$ melts at 47°, and, when anhydrous, at 122°. The *amide* melts at 199°. The

nitrile melts at 54° (B. **23,** 1577). The *oxime,* when acted upon with water, yields CO_2 and o-nitro-benzo-nitrile. Salicylic acid is produced when it is boiled with alkalies (B. **26,** 1252). It forms two isomeric *phenyl-hydrazones* (B. **28,** 2080).

m-Nitro-benzoyl-formic acid melts at 77°. The *amide* melts at 151°. The *nitrile* melts at 230° (145 mm.) (B. **14,** 1186).

p-Nitro-benzoyl cyanide, m.p. 116°, from iso-nitroso-p-nitro-benzyl cyanide by splitting (*J. pr. Ch.* 2, **66,** 353).

o-Amido-benzoyl-formic acid, *isatinic acid,* is produced on reducing o-nitro-benzoyl-formic acid with ferrous sulphate and sodium hydrate, and in the action of alkalies on isatin. If it be separated from its lead salt by means of hydrogen sulphide, and evaporated under greatly reduced pressure at low temperature, it is obtained as a white powder. Digestion of its solution converts it at once into its lactame or lactime—

Isatin, *lactame of isatinic acid* $C_6H_4\begin{cases}[1]CO.CO\\[2]NH\end{cases}$, or *lactime of isatinic acid* $C_6H_4\begin{cases}CO\\N\end{cases}C.OH$ (?), melting at 201°. It was first obtained by oxidising indigo. It consists of orange-red prisms. It dissolves in the caustic alkalies with the formation of salts. The solution, violet at first, soon becomes yellow, owing to the production of isatinates. Isatin acts at the same time like a ketone.

Its other methods of formation and its derivatives will be discussed later in connection with the hydro-indol derivatives. The isatin derivatives referable to the lactame formula are designated pseudo- or ψ-derivatives, or n-derivatives—*i.e.* those in which the recently entered group is attached to nitrogen,—whereas the true isatin derivatives are referred to the lactime formula, because the latter appears to belong to free isatin.

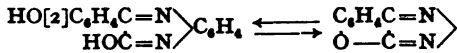
Aceto-isatinic acid $CH_3.CO.NH[2]C_6H_4.CO.CO_2H$, melting at 160°, results upon treating acetyl-ψ-isatin (see this) with alkalies, and then with acids. **Benzoyl-isatinic acid,** melting at 188°, is produced when benzoyl-tetrahydro-quinolin is oxidised with $KMnO_4$ (B. **24,** 772).

Acetyl-isatin $C_6H_4\begin{cases}[1]CO.CO\\[2]N-\end{cases}<_{CO.CH_3}$ melts at 141°. **Benzoyl-isatin** melts at 206°.

Anthroxanic acid $C_6H_4\begin{cases}[1]C-CO_2H\\[2]N>O\end{cases}$, m.p. 190°, is formed, with other products, during the oxidation of isatinic acid with Caro's acid, and by reduction of o-nitro-phenyl-glyoxalic acid with tin and glacial acetic acid; also by heating the o-nitroso-mandelic nitrile with concentrated HCl (B. **39,** 2344), and by oxidation of anthroxane-aldehyde with $KMnO_4$ (B. **16,** 2222; *J. pr. Ch.* 2, **81,** 254).

p-Dimethyl-amido-phenyl-glyoxylic ester $(CH_3)_2N.C_6H_4CO.CO_2C_2H_5$, m.p. 187°, is obtained from dimethyl-aniline ethyl-oxalic acid chloride, or oxalic ester with $AlCl_3$ (B. **10,** 2081; C. 1907, II. 310); the corresponding chloride results from dimethyl-aniline and oxalyl chloride. On heating, it decomposes into CO and **p-dimethyl-amido-benzoyl chloride** (B. **42,** 3486). p-Amino-phenyl-glyoxalic acid and its n-alkylated derivatives are also formed from the related amino-phenyl-tartronic acids by oxidation (C. 1901, I. 237, 239).

o-Oxy-phenyl-glyoxylic acid HO[2]C_6H_4COCOOH, m.p. 57°, from isatinic acid through its diazo-sulphate; the acid condenses with phenylene-diamine to o-oxy-phenyl-oxy-quinoxalin, which may be transformed into a lactone, the so-called cumaro-phenazin, and obtained from that (B. **34**, 2294):



o-Acetoxy-phenyl-glyoxylic acid, m.p. 101°–106°, with one molecule H_2O, is produced from its nitrile, m.p. 111°, the result of the action of silver cyanide upon acetyl-salicylic chloride (A. **368**, 80). The lactone corresponding to isatin—

Cumarandione $C_6H_4\langle\begin{smallmatrix}CO\\O\end{smallmatrix}\rangle CO$, in yellow needles, m.p. 178°, is obtained by the oxidation of the so-called oxindigo with CrO_3 in glacial acetic acid (B. **42**, 199). From it is derived iso-nitroso-cumaranone $C_6H_4\langle\begin{smallmatrix}CO\\O\end{smallmatrix}\rangle C:NOH$, melting at 172° with decomposition (B. **35**, 1640, 4346). The p-dimethyl-amido-anile of cumarandione $C_6H_4\langle\begin{smallmatrix}CO\\O\end{smallmatrix}\rangle C:NC_6H_4N(CH_3)_2$, m.p. 185°, is produced by the condensation of cumaranone with p-nitroso-dimethyl-aniline (B. **44**, 124).

Thio-isatin, *thio-naphthene-quinone* $C_6H_4\langle\begin{smallmatrix}CO\\S\end{smallmatrix}\rangle CO$, yellow prisms from alcohol, m.p. 121°, b.p. 247°, from its anile, the transformation product of dibromo-thio-indoxyl $C_6H_4\langle\begin{smallmatrix}CO\\S\end{smallmatrix}\rangle CBr_2$, and from iso-nitroso-thio-indoxyl $C_6H_4\langle\begin{smallmatrix}CO\\S\end{smallmatrix}\rangle C:NOH$, m.p. 172°, and by splitting up with dilute H_2SO_4. Dissolves in alkalies with formation of salts of thio-phenol-o-glyoxylic acid, which, in the free state, easily fall back into the anhydrides (B. **41**, 227).

p-Methoxy-phenyl-glyoxylic acid melts at 89°.

Veratroyl-carboxylic acid $(CH_3O)_2[3,4]C_6H_3.CO.CO_2H$, m.p. 138°, and **piperonoyl-carboxylic acid** $(CH_2O_2)[3,4]C_6H_3CO.CO_2H$, m.p. 148°, have been produced by the oxidation of anethol, of iso-eugenol-methyl ether, and of iso-safrol (B. **24**, 3488). The nitriles of the first two acids, m.p. 64° and 117°, are prepared from anisic acid chloride and veratroyl chloride and HCN respectively in the presence of pyridin (B. **42**, 188). 2, 5-dioxy-phenyl-glyoxylic acid, m.p. 141°, results from oxidation of o-oxy-phenyl-glyoxylic acid with K persulphate in alkaline solution (C. 1907, II. 901).

Homologous Phenyl-glyoxylic Acids.—m-Tolyl-glyoxylic acid yields so-called **methyl-isatin** $CH_3[5]C_6H_3\begin{cases}[1]CO\,.\,CO\\[2]NH\end{cases}$, m.p. 184°. This is obtained by boiling **p-methyl-isatin-p-tolyl-imide,** m.p. 259°, the product of the action of dichloro-acetic acid upon p-toluidin, with hydrochloric acid (B. **16**, 2262; **18**, 198).

p-Tolyl-glyoxylic acid . . .	m.p.	96°	(B. **14**, 1750; **20**, 2049).
(p-)[2, 5]-Xylyl-glyoxylic acid . . .	,,	75°	(C. 1898, I. 42).
(m-)[2, 4]-Xylyl-glyoxylic acid . . .	,,	85°	(*J. pr. Ch.* **2**, **41**, 485).
(o-)[2, 3]-Xylyl-glyoxylic acid . . .	,,	92°	(B. **20**, 1766).
Mesityl-glyoxylic acid . .	,,	112°–116°	(B. **24**, R. 741).
[2, 4, 5]-Pseudo-cumyl-glyoxylic acid .	,,	75°	(B. **24**, R. 741).

2, 3, 4, 6- and **2, 3, 5, 6-Tetramethyl-phenyl-glyoxylic acid** (B. **19,** 233; **20,** 3099). **Cymyl-glyoxylic acid** (C. 1898, I. 42).

Phenyl-pyro-racemic acid $C_6H_5.CH_2.CO.CO_2H$ melts at 154° with evolution of carbon dioxide. It is formed when α-benzoyl-amido-cinnamic acid (A. **275,** 8) is boiled with caustic alkali or hydrochloric acid, as well as by boiling phenyl-oxal-acetic ester with dilute sulphuric acid (A. **271,** 163). Ammonia converts it into α-phenacetyl-amido-hydro-cinnamic acid, or phenacetyl-phenyl-alanin. Oxidised with H_2O_2, in alkaline solution, it decomposes cleanly into CO_2 and phenyl-acetic acid (C. 1904, I. 194). With benzaldehyde and concentrated HCl it unites to form β, γ-diphenyl-α-keto-butyrol-acetone (A. **333,** 160).

o-Oxy-phenyl-pyro-racemic acid $HO.C_6H_4CH_2.CO.CO_2H$ is produced, like phenyl-pyro-racemic acid, from α-benzoyl-amido-o-oxy-cinnamic acid and sodium hydroxide. Its lactone, **α-oxo-hydro-cumarin** $C_6H_4\begin{cases}[1]CH_2.CO\\ [2]O\text{—}CO\end{cases}$ (?), m.p. 152°, is produced when it is boiled with acids (B. **18,** 1187).

Nitro-substituted phenyl-pyro-racemic acids are obtained synthetically by condensation of oxalic ester, and o- or p-nitro-toluols with sodium ethylate:

o-Nitro-phenyl-pyro-racemic acid $NO_2[2]C_6H_4CH_2COCOOH$, m.p. 121°, gives, on reduction, n-oxy-indol and, further, α-indol-carboxylic acid $C_6H_4\langle\begin{matrix}NH\\CH\end{matrix}\rangle CCOOH$. **p-Nitro-phenyl-pyro-racemic acid,** m.p. 194°; **o, p-** and **o, m-methyl-nitro-phenyl-pyro-racemic acid,** m.p. 145° and 193° (B. **30,** 1030; **31,** 387).

Benzyl-pyro-racemic acid $C_6H_5CH_2CH_2COCOOH+1\frac{1}{2}H_2O$, m.p. 47°, results from the transposition of α-oxy-phenyl-crotonic acid by means of NaHO, while HCl forms the isomeric benzoyl-propionic acid; further, benzyl-pyro-racemic acid is also obtained by splitting up benzoyl-oxal-acetic ester (A. **299,** 28; B. **31,** 3134).

B. **Phenyl-paraffin-β-ketone-carboxylic Acids** are produced (1) by a condensation, similar to the aceto-acetic ester formation, from benzoic and fatty acid esters, aceto-phenone, and carbonic acid esters, with alcohol elimination, in the presence of sodium alcoholate (see Benzoyl-acetic ester); (2) by the introduction of alphyl residues, by means of chlorides—*e.g.* benzyl chloride,—into aceto-acetic ester (see Benzyl-aceto-acetic ester); (3) by action of benzaldehydes upon diazo-acetic ester (see Benzoyl-acetic ester).; (4) from malonic ester acid chlorides and benzene, in presence of $AlCl_3$ (C. 1905, II. 30); (5) by transposition of benzoyl chloride or bromide with Mg-α-halogen aliphatic acid esters (A. **347,** 71); (6) by hydration of phenyl-propiolic acid ester.

With hydroxylamine they yield oxime anhydrides, lactoximes, or iso-azolones; and with hydrazin and phenyl-hydrazin, hydrazin anhydrides, lactazames, or pyrazolones.

Benzoyl-acetic acid $C_6H_5.CO.CH_2.CO_2H$, m.p. 103° with decomposition into CO_2 and aceto-phenone. It breaks down, in the same manner, when it is boiled with dilute acids. It is obtained by saponifying its ethyl ester with caustic potash at the ordinary temperature. Ferric chloride imparts a violet-red coloration to its solution.

Benzoyl-acetic ester $C_6H_5.CO.CH_2.CO_2C_2H_5$ boils at 148° (11 mm.). (1) It was first prepared by dissolving phenyl-propionic ester in sulphuric acid and then diluting with water (B. **17**, 66). (2) By the action of sulphuric acid and water upon α-bromo-cinnamic ester (B. **19**, 1392). (3) It is most conveniently made by the action of dry sodium ethylate or sodium upon ethyl benzoate and acetic ester (B. **20**, 653, 2179). (4) By splitting up benzoyl-acetic ester with ammonia (A. **291**, 70). (5) Small quantities of the ester are produced when esters of carbonic acid act upon aceto-phenone together with sodium ethylate. (6) It is also formed when benzaldehyde is heated with diazo-acetic ester. (7) From malonic ester acid chloride, benzene, and $AlCl_3$. (8) From benzyl bromide and magnesium-bromacetic ester :

1. $C_6H_4.C{=}C.CO_2C_2H_5$ —(SO_4H_2, H_2O)→
2. $C_6H_5.CH{=}CBr.CO_2C_2H_5$ —→
3. $C_6H_5.CO_2C_2H_5 + CH_3CO_2C_2H_5$ —($-C_2H_5OH$)→
4. $C_6H_5COCH(COCH_3)CO_2C_2H_5$ —($NH_3.H_2O$)→
5. $C_6H_5.CO.CH_3 + C_2H_5O.CO_2C_2H_5$ —→
6. $C_6H_5.CHO + N_2.CH.CO_2C_2H_5$ —($-N_2$)→
7. $C_6H_6 + ClCO.CH_2.CO_2C_2H_5$ —($AlCl_3$, $-HCl$)→
8. $C_6H_5COBr + BrCH_2CO_2C_2H_5$ —(Mg)→

→ $C_6H_5.CO.CH_2CO_2C_2H_5$ Benzoyl-acetic ester.

Benzoyl-acetic ester volatilises with steam without decomposition (A. **282**, 155). Its odour resembles that of aceto-acetic ester.

It forms (1) with ammonia an addition product like that of aldehyde-ammonia ; with amines it splits off water and yields imides—*e.g.* **β-methyl-imido-hydro-cinnamic ester** $C_6H_5C(NCH_3)CH_2.CO_2.C_2H_5$ (B. **29**, 105) ; (2) with hydrazin it yields 3-phenyl-pyrazolone ; (3) with phenyl-hydrazin, diphenyl-pyrazolone ; (4) with hydroxylamine, phenyl-isoxazolone ; (5) with urea, phenyl-uracile ; (6) with guanidin, imido-phenyl-uracile ; (7) with nitrous acid, the oxime ; (8) with diazo-benzene chloride, the phenyl-hydrazone of benzoyl-glyoxylic ester ; (9) with PCl_5, β-chloro-cinnamic chloride. Iodine converts its sodium compound into dibenzyl-succinic ester, while with the alkylogens homologous benzoyl-acetic esters result. The hydrogen atoms of the CH_2 group are also replaceable, step by step, by acid radicles. It yields β-ethoxy-cinnamic esters when acted upon with orthoformic esters. The *amide* melts at 112° (A. **266**, 332), and the *anilide* at 107° (A. **245**, 374).

The dimethyl-acetal $C_6H_5C(OCH_3)_2CH_2CO_2CH_3$, b.p.$_{16}$ 147°, is formed from phenyl-propiolic acid methyl ester with alcoholic Na methylate solution at 125° (C. 1903, II. 664) ; diethyl-acetal, b.p.$_{13}$ 153° (C. 1904, I. 659).

Benzoyl-aceto-nitrile, *R-cyanaceto-phenone* $C_6H_5.CO.CH_2.CN$, melting at 80°, is produced on boiling benzoyl-cyanacetic ester with water, on acting upon sodium oxy-methylene-aceto-phenone with hydroxylamine hydrochloride and sodium hydroxide (B. **24**, 133), and upon treating imido-benzoyl-aceto-nitrile or imido-benzoyl-methyl cyanide with hydrochloric acid.

Imido-benzoyl-cyano-methane $C_6H_5.C(:NH)CH_2CN$, melting at 86°, results when sodium acts upon a dry ethereal solution of benzo-

nitrile and methyl cyanide or aceto-nitrile (B. **22**, R. 327). When treated with hydroxylamine hydrochloride, the imido-group is replaced by the oximido-group, and the latter adds itself to cyanogen with the production of **phenyl-isoxazolonimide** $\begin{matrix} N\text{——}O \\ \| \quad | \\ C_6H_5C.CH_2.C:NH \end{matrix}$, melting at 111° (B. **26**, R. 272).

p-Nitro-benzoyl-acetic acid $C_6H_4(NO_2).CO.CH_2.CO_2H$ melts at 135°, and is produced by heating p-nitro-phenyl-propiolic ester with sulphuric acid. It breaks down, on melting, into CO_2 and p-nitro-aceto-phenone. o-Nitro-phenyl-propiolic ester is readily transposed into the isomeric isatogenic ester (B. **17**, 326).

o-, m-, and p-Nitro-benzoyl-acetic esters (liquid, m.p. 79° and 75° respectively) are best prepared by splitting up the corresponding nitro-benzoyl-aceto-acetic esters (B. **35**, 931, 933 ; C. 1904, I. 724).

Methyl-benzoyl-acetic ester, boiling at 226° (225 mm.), when treated with nitrous acid forms α-iso-nitroso-propio-phenone (B. **21**, 2119). **α-Ethyl-** and **diethyl-benzoyl-acetic ester** boil at 210° (90 mm.) and 223° (150 mm.).

Allyl-benzoyl-acetic ester boils at 220° (100 mm.). **Benzoyl-trimethylene-carboxylic acid,** melting at 148°, decomposes at higher temperatures into CO_2 and *benzoyl-trimethylene* (pp. 268 *seq.*) (B. **16**, 2128, 2136).

α-Phenyl-aceto-acetic ester $C_6H_5CH(COCH_3)COOC_2H_5$, b.p.$_{11}$ 146°, is obtained by saponifying its nitrile, m.p. 90°, a condensation product of benzyl cyanide and acetic ester, by means of sodium ethylate (B. **31**, 3160) ; similarly, we obtain **propionyl-phenyl-acetic ester** $C_6H_5CH(COCH_2CH_3)CO_2C_2H_5$, b.p.$_{18}$ 155°, and **propionyl-benzyl cyanide,** m.p. 70° (B. **36**, 2242).

2, 5-Dinitro-phenyl- and **2, 4, 6-trinitro-phenyl-aceto-acetic ester,** melting at 94° and 98°, result from the action of 2, 5-dinitro-bromo-benzene and 2, 4, 6-trinitro-chloro-benzene upon sodium aceto-acetic ester (A. **220**, 131 ; B. **22**, 990 ; **23**, 2720).

Benzyl-aceto-acetic ester $C_6H_5.CH_2.CH\begin{matrix} CO.CH_3 \\ CO_2CH_3 \end{matrix}$ is derived from sodium aceto-acetic ester and benzyl chloride (A. **204**, 179). It boils at 276°, and by the ketone decomposition yields benzyl-acetone (B. **15**, 1875) ; by the acid decomposition it forms phenyl-propionic acid.

C. **γ- and δ-Ketone-carboxylic Acids** $C_6H_5.CO.CH_2.CH_2.CO_2H$, m.p. 116°, are obtained (1) by the condensation of benzene and succinic anhydride by means of $AlCl_3$ (B. **20**, 1376) ; (2) by condensation of benzaldehyde with maleïc acid, or fumaric acid, by means of piperidin at 150°–160° (C. 1903, I. 769) ; (3) by reducing β-benzoyl-acrylic acid ; (4) by the elimination of carbon dioxide from benzoyl-iso-succinic acid, and (5) from phenacyl-benzoyl-acetic ester by the acid decomposition ; (6) by boiling the HCN addition product of cinnamic aldehyde with dilute hydrochloric acid, and carefully saponifying the phenyl-oxy-crotonic acid produced at first when cold, which with heat rearranges itself (B. **29**, 2582 ; A. **299**, 23) :

$$C_6H_5CH:CH.CH(OH)CN \longrightarrow C_6H_5CH:CH.CH(OH)COOH \longrightarrow C_6H_5CO.CH_2.CH_2COOH.$$

(7) Benzoyl-propionic acid is also formed by transposition of γ-phenyl-α-oxy-butyro-lactone (B. **36**, 2529).

By splitting off H_2O it yields **phenyl-Δ^2-croto-lactone** $C_6H_5\overline{C:CH.CH_2COO}$, m.p. 91°. From the dibromide of cinnamic aldehyde cyano-hydrin the isomeric oily **phenyl-Δ^1-croto-lactone** is obtained, $C_6H_5.\overline{CH.CH:CH.COO}$, which easily transposes into the Δ^2-lactone (A. **319**, 196).

Reduction transforms β-benzoyl-propionic acid into γ-phenyl-butyro-lactone.

Phosphorus pentasulphide converts the acid into phenyl-oxy-thiophene (B. **19**, 553). It yields two isomeric *oximes*, melting at 129° and 92° (B. **25**, 1932).

α-Methyl-β-benzoyl-propionic acid $C_6H_5COCH_2CH(CH_3)COOH$, m.p. 136°, by condensation of benzene and pyro-tartaric anhydride with $AlCl_3$ (C. 1900, II. 172).

γ-Benzoyl-butyric acid $C_6H_5COCH_2CH_2CH_2COOH$, m.p. 126°, from glutaric acid chloride with benzene and $AlCl_3$, as well as α-benzoyl-glutaric ester by ketone-fission (B. **31**, 2001).

α-Phenyl-lævulinic acid $C_6H_5.CH\langle^{CO_2H}_{CH_2.CO.CH_3}$, m.p. 126°, is derived from phenyl-aceto-succinic ester (B. **17**, 72; **18**, 790). **β-Benzyl-lævulinic acid** $C_6H_5.CH_2.CH\langle^{CH_2.CO_2H}_{CO.CH_3}$, from β-benzal-lævulinic acid (A. **254**, 202), m.p. 98°. See Benzal-angelica-lactone. **β-Phenyl-γ-aceto-butyric acid** $C_6H_5.CH\langle^{CH_2.CO_2H}_{CH_2.CO.CH_3}$, m.p. 83°. It is obtained from phenyl-dihydro-resorcin by the action of alkalies or acids (B. **26**, 2057; A. **294**, 322). Phenyl-dihydro-resorcin is again formed when its esters are condensed with sodium alcoholate.

(9) Phenyl-alcohol-ketone-carboxylic Acids.

Benzoyl-glycollic acid $C_6H_5.CO.CH(OH)CO_2H$, m.p. 125° (B. **16**, 2133).

α-Acidyl-phenyl-glycollic esters like **p-toly-acetyl-glycol-methyl ester** $CH_3C_6H_4C(OH)(COCH_3).CO_2CH_3$, b.p.$_{15}$ 190°, and **p-dimethyl-amido-phenyl-acetyl-glycollic-methyl ester** $(CH_3)_2NC_6H_4C(OH)(COCH_3)CO_2CH_3$, m.p. 81°, etc., are formed by condensation of aromatic hydrocarbons and anilines with α, β-diketo-butyric ester (C. 1909, I. 1795). They are easily reduced to the corresponding aldehydes.

Acetoxy-phenyl-pyro-racemic nitrile $C_6H_5CH(O.COCH_3).CO.CN$, m.p. 52·5°, b.p.$_{10}$ 150°, by heating acetyl-mandelic chloride with silver cyanide (A. **368**, 77). Derived from **phenyl-oxy-pyro-racemic acid** is the acid $C_6H_5CH(NHC_6H_5)C\langle^{OH}_{N:CHC_6H_5}COOH$, m.p. 194°, whose nitrile is obtained by condensation of phenyl-anilido-acetic nitrile with benz-aldehyde and KCN (B. **29**, 1732; **31**, 2701).

γ-Phenyl-γ-keto-α-oxy-butyric acid $C_6H_5.CO.CH_2.CH(OH)CO_2H$, m.p. 125°, is obtained from its trichloride, chloral-aceto-phenone $C_6H_5.CO.CH_2.CH(OH)CCl_3$, m.p. 76° (B. **26**, 557).

From the geometrically isomeric phenyl-keto-oxy-butyric acids are derived the bromination products of phenyl-aceto-acetic ester, and α-propionyl-phenyl-acetic ester: **α-bromo-phenyl-acetic ester** CH_3CO

$CBr(C_6H_5)CO_2C_2H_5$ and **α-propionyl-phenyl-bromo-acetic ester** $CH_3CH_2COCBr(C_6H_5)CO_2C_2H_5$; also **γ-bromo-phenyl-acetic ester** $CH_2BrCOCH(C_6H_5)CO_2C_2H_5$ and **γ-bromo-propionyl-phenyl-acetic ester** $CH_3CHBrCOCH(C_6H_5)CO_2C_2H_5$. The first two, distilled with steam, disintegrate into CO, HBr, and atropic acid ester or β-methyl-atropic acid ester; the last two, on heating with water, yield lactones, viz., **α-phenyl-tetronic acid** $\overline{CH_2.C(OH):C(C_6H_5)COO}$, m.p. 254°, and **α-Phenyl-γ-methyl-tetronic acid** $CH_3\overline{CH.C(OH):C(C_6H_5)COO}$, m.p. 178° (B. **39**, 3929). **γ-Phenyl-tetronic acid** $C_6H_5\overline{CH.C(OH):CH.COO}$, m.p. 128°, is formed from the transformation product of acetyl-mandelic chloride with sodium-malonic ester, by saponification and elimination of CO_2 (A. **368**, 65).

(10) Diketone-carboxylic Acids.

Benzoyl-glyoxylic acid $C_6H_5.CO.CO.CO_2H$. The ethyl ester, an orange-coloured oil, boiling at 150°–153° (13 mm.), is formed by conducting N_2O_3 into a mixture of benzoyl-acetic ester and acetic anhydride. With water and alcohols it forms colourless hydrates and alcoholates (C. 1907, II. 233).

The α-oxime and α-phenyl-hydrazone, of the ethyl ester of this acid, have been prepared by the action of nitrous acid and diazo-benzol chloride (B. **21**, 2120) upon benzoyl-acetic ester.

Benzoyl-iso-nitroso-acetic ester $C_6H_5.CO.C(:NOH)CO_2C_2H_5$, m.p. 121°. **Benzoyl-α-phenyl-hydrazone-glyoxylic ester** $C_6H_5.CO.C(:NNHC_6H_5)CO_2C_2H_5$, m.p. 65°. The benzoyl-amido-acetic ester obtained by reduction of benzoyl-iso-nitro-acetic ester yields on diazotising **benzoyl-acetic ester diazo-anhydride** $\begin{matrix}C_6H_5C.O\\CO_2RC.N\end{matrix}\!\!>\!\!N$ (B. **36**, 3612).

Quinisatinic acid, o-amido-benzoyl-glyoxylic acid $NH_2[2]C_6H_4CO.CO.CO_2H$ at 120° breaks down into water and its lactame or lactime. It is obtained by oxidising β, γ-dioxy-carbo-styrile with ferric chloride. Its lactame or lactime is—

Quinisatin $C_6H_4\begin{cases}[1]CO.CO\\|\\[2]NH.CO\end{cases}$ or $C_6H_4\begin{cases}[1]CO.CO\\|\\[2]N=COH\end{cases}$, m.p. 255°–260° (B. **17**, 985).

Benzoyl-pyro-racemic acid $C_6H_5.CO.CH_2.CO.CO_2H$, m.p. 157°, is prepared from its **ethyl ester** (melting at 43°), produced in the condensation of aceto-phenone and oxalic acid (B. **21**, 1131). Ferric chloride imparts a blood-red colour to the alcoholic solution of the ester. Benzoyl-pyro-racemic chloralide, see B. **31**, 1306. Nucleus-substituted benzoyl-pyro-racemic esters, see B. **34**, 2477; **36**, 2695.

When benzoyl chloride acts upon aceto-acetic ester, it produces **benzoyl-aceto-acetic ester** $C_6H_5.CO.CH.(CO.CH_3).CO_2C_2H_5$. This decomposes into aceto-phenone and benzoyl-acetone (B. **18**, 2131).

o-, m-, and **p-Nitro-benzoyl-aceto-acetic ester** (A. **221**, 323; B. **35**, 931, 933).

Aceto-phenone-aceto-acetic ester $C_6H_5.CO.CH_2.CH.\begin{matrix}CO_2H\\CO.CH_3\end{matrix}$ melts at 130°–140°, with decomposition into CO_2 and aceto-phenone-acetone. Its *ethyl ester* is produced by the action of ω-bromo-aceto-

phenone upon sodium aceto-acetic ester (B. **16,** 2866). Like aceto-phenone-acetone, the ester readily forms a furfurane derivative. On treatment with alcoholic potash it passes into γ-phenyl-α-acetyl-crotonic lactone.

θ-Phenacyl-lævulinic acid, see B. **34,** 1263.

(11) Phenyl-paraffin-dicarboxylic Acids.

The phenyl-paraffin-dicarboxylic acids, like the aliphatic, saturated dicarboxylic acids, can be arranged into malonic acids, ethylene-succinic acids, etc.

Phenyl-malonic Acids.—**Phenyl-malonic acid** $C_6H_5.CH(CO_2H)_2$ melts at 152°, splitting off CO_2 and forming phenyl-acetic acid. Its *ester*, boiling at 171° (14 mm.), is formed from phenyl-oxalacetic ester by the elimination of carbon monoxide (B. **27,** 1091). **Dinitro-phenyl-malonic ester** $(NO_2)_2.C_6H_3.CH(CO_2C_2H_5)_2$, melting at 51°, is obtained by the action of bromo-dinitro-benzene upon sodium malonic ester (B. **21,** 2472; **22,** 1232; **23,** R. 460; **26,** R. 10).

2, 4, 6-Trinitro-phenyl-malonic ester, *picryl-malonic ester* $(NO_2)_3C_6H_2CH(CO_2C_2H_5)_2$, exists in two modifications, melting at 58° and 64° (B. **28,** 3066; **29,** R. 997; C. 1899, II. 25). **Bromo-thymo-quinone-malonic ester** $[C_6O_2Br(C_3H_7)]CH(CO_2C_2H_5)_2$, m.p. 78°, gives blue salts with metals (B. **34,** 1558).

Phenyl-cyano-acetic acid $C_6H_5CH(CN).COOH$, m.p. 92°. Its ethyl ester, b.p. 275°, is formed by the action of Na and carbonic acid ester upon benzyl cyanide. The amide, m.p. 147°, gives, on treatment with PCl_5, **phenyl-malonic nitrile** $C_6H_5CH(CN)_2$, m.p. 69°, b.p.$_{21}$ 153° (C. 1904, II. 953).

Benzyl-malonic acid, *β-phenyl-iso-succinic acid* $C_6H_5.CH_2.CH(CO_2H)_2$, melting at 117°, is obtained from its ester, produced in the action of benzyl chloride upon sodium-malonic ester, as well as by the reduction of benzal-malonic acid (A. **218,** 139).

o- and **p-Nitro-benzyl-malonic ester** (B. **20,** 434). The o-acid is condensed by sodium hydroxide to n-oxy-α-indol-carboxylic acid (B. **29,** 639). **Methyl-benzyl-malonic acid** (A. **204,** 177). **β-Phenyl-ethyl-malonic-acid ester** $C_6H_5(CH_3)CH.CH(COOC_2H_5)_2$, b.p.$_{15}$ 230°, by attachment of CH_3MgI to benzal-malonic ester. The acid melts at 144° with decomposition into CO_2 and β-phenyl-butyric acid (C. 1905, II. 1023).

Phenyl-succinic Acids.—**Phenyl-succinic acid** $\begin{matrix} C_6H_5.CH.CO_2H \\ | \\ CH_2.CO_2H \end{matrix}$, melting at 167°, results from ω-chloro-styrol $C_6H_5.CH:CHCl$, as well as from benzal-malonic ester, by means of potassium cyanide (A. **293,** 338); by the decomposition of phenyl-aceto-succinic ester, by means of very concentrated caustic potash; from phenyl-ethane-tricarboxylic acid, and from the so-called hydro-corniculatic acid $C_{17}H_{16}O_8$. Its *anhydride* melts at 54° (B. **28,** R. 573), and another modification at 150° (M. **24,** 413; C. 1907, I. 720). Chloride, b.p.$_{12}$ 151°. Dimethyl ester, m.p. 58°, b.p.$_{12}$ 161°.

Ester Acids.—By semi-esterification of phenyl-succinic acid, or attachment of methyl alcohol to the anhydride, we get about 75 per cent. **phenyl-succinic β-methyl-ester α-acid** $C_6H_5CH(CO_2H).CH_2CO_2$

CH_3, m.p. 92°, and about 25 per cent. **phenyl-succinic α-methyl-ester β-acid** $C_6H_5CH(CO_2CH_3).CH_2CO_2H$, m.p. 103°.

Pure α-methyl ester β-acid is obtained by semi-saponification of the neutral ester, and the β-methyl ester α-acid from **β-phenyl-β-cyano-propionic methyl ester** $C_6H_5.CH(CN).CH_2CO_2CH_3$, m.p. 55°, by saponification of the cyanogen group. The constitution of the two isomeric ester acids follows from the transformation of the ester acid chlorides with benzene and $ACCl_3$, whereby the β-methyl ester α-acid passes into desyl-acetic ester and the α-methyl β-acid into phenyl-phenacyl-acetic ester (A. **354,** 117).

Phenyl-succinic β-amido-α-acid $C_6H_5CH(COOH).CH_2CONH_2$, m.p. 145°, formed by attachment of NH_3 to the anhydride, the isomeric **phenyl-α-amido-β-acid** $C_6H_5CH(CONH_2).CH_2COOH$, m.p. 159°, from **β-phenyl-β-cyano-propionic acid** (*q.v.*).

o-Oxy-phenyl-succinic acid melts with decomposition at 150°. It is obtained from cumarin and potassium cyanide (A. **298,** 366).

Phenyl-methyl-succinic acids $\begin{matrix} C_6H_5.CH.CO_2H \\ | \\ CH_3.CHCO_2H \end{matrix}$ have been obtained in two modifications, melting at 170° and 192° (B. **24,** 1876).

Benzyl-succinic acid $\begin{matrix} C_6H_5.CH_2.CH.CO_2H \\ | \\ CH_2.CO_2H \end{matrix}$ melts at 161°, and results from sodium ethan-tricarboxylic ester, or sodium ethan-tetra-carboxylic ester by the action of benzyl chloride, etc. (B. **17,** 449), as well as by the reduction of phenyl-itaconic acid (B. **23,** R. 237). It forms an *anhydride*, melting at 102°.

Phenethyl-succinic acid $C_6H_5CH_2CH_2CH(COOH)CH_2COOH$, m.p. 136°, by reduction of styryl-succinic acid, and from hydro-cinnamyl-idene-malonic acid, with KCN.

Phenyl-glutaric Acid.—**α-Phenyl-glutaric acid** $C_6H_5CH(COOH)CH_2CH_2COOH$, m.p. 83°, from $C_6H_5CH(COOR)CH_2CH(COCH_3)COOR$ or $C_6H_5C(COOR)_2CH_2CH_2COOR$ by splitting; easily passes into the anhydride, m.p. 95° (B. **34,** 4175).

β-Phenyl-glutaric acid $C_6H_5CH(CH_2COOH)_2$, m.p. 142°, by splitting up β-phenyl-propane-$\alpha\alpha_1$-tri- or tetracarboxylic ester, the condensation products of cinnamic ester, or benzol-malonic ester, with malonic ester by means of sodium ethylate. By nitration it is transformed into a mixture of **o-, m-,** and **p-nitro-phenyl-glutaric acids,** m.p. 205°, 204°, and 240°. The o-nitro-acid gives, on reduction with $SnCl_2$ and HCl, **hydro-carbo-styrile-γ-acetic acid** $C_6H_4\begin{cases}[1]CH(CH_2COOH).CH_2 \\ [2]NH\text{———}CO\end{cases}$, m.p. 183° (B. **40,** 1586). Homologous and substituted β-phenyl-glutaric acids, see A. **360,** 344. **β-Phenyl-α-methyl-glutaric acid,** m.p. 125°, from the result of attaching methyl-malonic ester to benzal-malonic ester.

(12) Phenyl-alcohol-dicarboxylic Acids.

A general method for preparing these substances consists in the condensation of aromatic hydrocarbons, anilines, and phenols, and mesoxalic acid ester or alloxane (all in one), under the influence of concentrated sulphuric acid (C. 1909, I. 1560). They are easily oxidised to the corresponding phenyl-glyoxylic acids and aromatic aldehydes (see C. 1910, I. 25).

Phenyl-tartronic methyl ester $C_6H_5C(OH)(CO_2CH_3)_2$, m.p. 67°, b.p.$_{11}$ 165°; **p-tolyl-tartronic methyl ester,** m.p. 72°; **p-methoxy-** and **p-dimethyl-amido-phenyl-tartronic methyl ester** melt at 118° and 115°.

Trinitro-phenyl-tartronic ester $(NO_2)_3C_6H_2C(OH)(CO_2C_2H_5)_2$, m.p. 117°, by oxidation of trinitro-phenyl-malonic ester with HNO_3 (C. 1899, II. 25).

Benzyl-tartronic acid $C_6H_5.CH_2.C(OH)(CO_2H)_2$ melts at 143°, with decomposition into CO_2 and β-phenyl-lactic acid. It results from the action of caustic potash on *benzyl-chloro-malonic ester*, the product obtained from the interaction of benzyl chloride and sodium chloro-malonic ester (A. **209,** 243). *α Anilido-, phenyl-hydrazido-benzyl-malonic ester*, etc., are produced by the addition of the respective bases to benzal-malonic ester (B. **28,** 1451; **29,** 813).

β-Methoxy-benzyl-malonic acid $C_6H_5.CH(OCH_3).CH(CO_2H)_2$ melts at 115° with decomposition into methyl alcohol and benzal-malonic acid, from whose ester the β-methoxy-benzyl-malonic ester is produced by addition of sodium methylate (B. **27,** 289).

Phenyl-malic Acids.—α-Phenyl-α-oxy-succinic acid $\begin{matrix} C_6H_5.C(OH)CO_2H \\ | \\ CH_2\ .\ CO_2H \end{matrix}$, m.p. 187°, is produced by the action of bromine, phosphorus, and water upon phenyl-succinic acid.

α-Phenyl-β-oxy-succinic acid $\begin{matrix} C_6H_5.CH.CO_2H \\ | \\ CH(OH).CO_2H \end{matrix}$, m.p. 150°–160°, results from the interaction of phenyl-formyl-acetic ester, prussic acid, and hydrochloric acid (B. **23,** R. 573).

Benzyl-malic acid $\begin{matrix} C_6H_5CH_2CHCO_2H \\ CH(OH)CO_2H \end{matrix}$, m.p. 155°, from the condensation product of chloral with benzyl-malonic acid by saponification with KOH (B. **38,** 2737).

Phenyl-itamalic acid may be obtained in the form of its *lactone acid*, **phenyl-paraconic acid** $\begin{matrix} C_6H_5.CH.CH\text{—}CO_2H \\ | \quad\quad\quad \diagdown CH_2 \\ O\text{—}CO \end{matrix}$, m.p. 109°, by heating benzaldehyde with sodium succinate and acetic anhydride (A. **256,** 63). For other methods, see B. **33,** 1294; A. **321,** 127; **330,** 292.

Phenyl-paraconic acid, upon distillation, breaks down into carbon dioxide, phenyl-butyro-lactone, and phenyl-iso-crotonic acid. A further product is *α-naphthol* (*q.v.*).

Phenyl-itaconic acid is produced when metallic sodium, or sodium ethylate, acts upon phenyl-paraconic esters. Hydriodic acid reduces it to benzyl-succinic acid and phenyl-butyric acid (B. **29,** 15).

o-, m-, and **p-Chloro-phenyl-paraconic acids** result from the condensation of monochloro-benzaldehydes with sodium succinate, and yield three chlorinated naphthols (B. **21,** R. 733). **1, 3, 4-Dichloro-phenyl-paraconic acid,** m.p. 138°, forms two dichloro-naphthols (B. **28,** R. 244).

α- and **β-Methyl-phenyl-paraconic acids** are produced in the condensation of benzaldehyde with pyro-tartaric acid, and yield methyl-α-naphthols (A. **255,** 257).

α-Phenyl-γ-valero-lactone-carboxylic acid $\begin{matrix} C_6H_5.CH.CO \diagdown \\ CO_2H.CH.CH\text{—}CH_2 \end{matrix} \diagup O$, m.p. 167°, is produced in the reduction of phenyl-aceto-succinic ester

(B. **18,** 791). **δ-Phenyl-δ-valero-lactone-γ-carboxylic acid,** m.p. 161°, by reduction of α-benzoyl-glutaric acid, on distillation, gives Δ^3-dihydro-cinnamenyl-acrylic acid.

(13) PHENYL-KETONE-DICARBOXYLIC ACIDS.

Benzoyl-malonic ester $C_6H_5.CO.CH(CO_2.C_2H_5)_2$ and **o-nitro-benzoyl-malonic ester** are produced by the action of benzoyl chloride and o-nitro-benzoyl chloride upon sodium-malonic ester (B. **20,** R. 381). The latter yields quinolin derivatives upon reduction (B. **22,** 386).

Benzoyl-cyano-acetic methyl ester $C_6H_5.CO.CH\langle^{CO_2.CH_3}_{CN}$, m.p. 74°, is formed from cyano-acetic methyl ester and benzoyl chloride. Its **ethyl ester,** m.p. 41°, from benzoyl-acetic ester and cyanogen chloride, yields cyano-aceto-phenone on boiling with water.

Phenyl-acetyl-malonic ester $C_6H_5CH_2.CO.CH(COOC_2H_5)_2$, from phen-acetyl chloride and Na-malonic ester, is condensed by concentrated H_2SO_4 to *naphtho-resorcin-carboxylic ester* (A. **298,** 374).

Benzoyl-iso-succinic ester $C_6H_5.CO.CH_2.CH(CO_2C_2H_5)_2$ is obtained from ω-bromaceto-phenone and sodium-malonic ester (B. **18,** 3324).

α-Benzoyl-glutaric ester $C_6H_5COCH(CO_2C_2H_5)CH_2CH_2CO_2C_2H_5$, b.p.$_{12}$ 200°–210°, from Na-benzoyl-acetic ester with β-iodo-propionic ester.

β-Benzoyl-glutaric acid $C_6H_5COCH(CH_2COOH)_2$, m.p. 122°, on stronger heating, gradually splits off H_2O and passes into the dilactone $C_6H_5C(-O-CO)-CH\langle^{CH_2.COO}_{CH_2.COO}$, m.p. 137°. The latter is formed synthetically from benzoic anhydride and sodium tricarbalkylate at 135°–140° with rejection of CO_2 and H_2O; it can easily be broken up into β-benzoyl-glutaric acid, and is reduced by sodium amalgam to phenyl-butyro-lactone-acetic acid $C_6H_5CH.CH(CH_2COOH)CH_2COO$, m.p. 114° (A. **314,** 58).

Phenyl-oxalacetic ester $\begin{matrix}C_6H_5.CH.CO.CO_2.C_2H_5\\ |\\ CO_2.C_2H_5\end{matrix}$ is formed from oxalic ester, phenyl-acetic ester, and sodium (B. **20,** 592). See Phenyl-malonic acid.

Phenyl-cyano-pyro-racemic ester $\begin{matrix}C_6H_5.CH.CO.CO_2C_2H_5\\ |\\ CN\end{matrix}$ is obtained from oxalic ester, benzyl cyanide, and sodium (A. **271,** 172). See Phenyl-pyro-racemic acid.

Phenyl-aceto-succinic ester $\begin{matrix}C_6H_5.CH.CO_2H\\ |\\ CH_3.CO.CH.CO_2H\end{matrix}$ is formed from sodium aceto-acetic ester and phenyl-bromacetic ester (B. **17,** 71).

Benzyl-aceto-succinic ester $\begin{matrix}C_6H_5.CH_2.CH.CO_2H\\ |\\ CH_3.CO.CH.CO_2H\end{matrix}$ results from the interaction of sodium aceto-succinic ester and benzyl chloride (B. **11,** 1058).

Benzyl-oxalacetic ester $\begin{matrix}C_6H_5CH_2CHCO_2C_2H_5\\ |\\ COCO_2C_2H_5\end{matrix}$, an oil, from oxalic ester, with hydro-cinnamic ester and Na alcoholate (B. **31,** 554).

(14) PHENYL-OXY-KETONE-DICARBOXYLIC ACIDS.

Keto-phenyl-paraconic ester $\begin{matrix} C_6H_5.CH.CH—CO_2C_2H_5 \\ | \quad\quad \rangle CO \\ O—CO \end{matrix}$ (B. **26,** 2144).

α-Benzoyl-δ-chloro-γ-valero-lactone $\begin{matrix} CO——O \\ | \quad\quad | \\ C_6H_5COCHCH_2.CH.CH_2Cl \end{matrix}$, m.p. 106°, from Na-benzoyl-acetic ester with epichloro-hydrin, is split up by alkali into benzoic acid and γ, δ-dioxy-valerianic acid, or into CO_2 and **benzoyl-butane-diol** $C_6H_5.CO.CH_2.CH_2.CH(OH).CH_2OH$, m.p. 91° (C. 1901, II. 237).

(15) PHENYL-PARAFFIN-TRICARBOXYLIC ACIDS.

Phenyl-carboxyl-succinic acid, phenyl-ethane-tricarboxylic acid.— Its ester is formed when phenyl-chloracetic ester acts upon sodium-malonic ester (A. **219,** 31). The acid breaks down, on heating, into CO_2 and phenyl-succinic acid (B. **23,** R. 573).

α, **β-Dicyano-β-phenyl-propionic ethyl ester** $C_6H_5CH(CN).CH(CN).CO_2C_2H_5$, m.p. 68°, by condensation of mandelic acid nitrile with sodium-cyano-acetic ester (C. 1906, II. 1563).

α-Phenyl-tricarballylic acid $C_6H_5CH(COOH).CH(COOH)CH_2COOH$, m.p. 110°, by saponification of the reaction products of KCN and phenyl-itaconic acid ester (C. 1903, II. 496).

Phenyl-butane-tricarboxylic acid $\begin{matrix} C_6H_5.CH.CH_2CO_2H \\ CH(CO_2H)CH_2CO_2H \end{matrix}$, trans-form ($+\frac{1}{2}H_2O$), m.p. 195°; cis-form, m.p. 179°, by saponification, and CO_2, elimination from the condensation product of cinnamic ester with Na-cyano-acetic ester and bromo-acetic ester; both acids yield the same anhydride acid, m.p. 135° (C. 1899, II. 833). The same structure is ascribed to the tricarboxylic acid obtained by attaching cinnamic acid to succinic acid ester, m.p. 200° with decomposition, which, however, has quite different properties (A. **315,** 219).

β-Phenyl-pimelin-β_1-acaric acid $\begin{matrix} C_6H_5CH.CH_2CO_2H \\ CH_2.CH(CH_2CO_2H)_2 \end{matrix}$, m.p. 142°, obtained from the condensation product of cinnamic aldehyde with three molecules sodium-malonic ester, by saponification with concentrated HBr (A. **360,** 337).

(16) PHENYL-KETO-TRICARBOXYLIC ACIDS.

α- and **β-Benzoyl-tricarballylic acids** $C_6H_5.CO.CH(COOH)CH(COOH)CH_2COOH$ and $C_6H_5COC(COOH)(CH_2COOH)_2$. Their esters are formed from chloro-succinic ester and benzoyl-acetic ester, or from benzoyl-acetic ester with bromo-acetic ester and sodium ethylate (B. **29,** R. 788).

(17) POLYKETO-POLYCARBOXYLIC ACIDS.

(17) By condensation of benzaldehydes, and substitution benzaldehydes with aceto-acetic esters, and similar substances, in the presence of aliphatic amines, several polyketo-polycarboxylic acids of the aromatic series have been obtained, which are interesting partly by their isomeric forms, and partly on account of their capacity for further condensations. It is, however, doubtful whether these compounds still contain the open aliphatic chain, or whether they

ought to be regarded as cyclic-ketone-alcohol-carboxylic acids of the hydro-aromatic series (A. **323,** 83; **332,** 22). Benzylidene-bis-aceto-acetic ester $C_6H_5CH[CH(COCH_3)CO_2C_2H_5]_2$ (?) is obtained from benz-aldehyde with two molecules aceto-acetic ester in three stereo-isomeric keto-forms—β, m.p. 150°; β_2, m.p. 154°; and β_3, m.p. 108°,—which, through their sodium salts, can be converted into the keto-enol forms—α, m.p. 61°; α_2, liquid; α_3, m.p. 65°–67°. The benzylidene-bis-aceto-acetic ester is easily condensed with elimination of H_2O to a cyclo-hexanone derivative (A. **313,** 129).

Addendum.—A number of compounds attach themselves to the phenyl-poly-alcohols and their oxidation products. They may be regarded as derived from the various classes of bodies which have just been described, by assuming, in addition to the one aliphatic side chain, a second or more groups (mostly carboxyl groups) attached to the benzene ring. Most of the bodies belonging here are o-di-derivatives of benzene, o-phenylene derivatives, obtained in part from o-phthalic acid, and in part by the oxidation of derivatives of ortho-condensed hydrocarbons—*e.g.* indene and naphthalene. Mention may be made of the subjoined compounds. Some of them are intimately related to the dicarboxylic acids, which have been discussed, carrying the one carboxyl group in the nucleus and the other in the side chain.

(18) PHENYLENE-OXY-DICARBOXYLIC ACIDS.

o-Carbo-mandelic acid $CO_2H[2]C_6H_4.CH(OH)CO_2H$ decomposes readily into water and a lactone-carboxylic acid:

Phthalide-carboxylic acid $C_6H_4\begin{cases}CH.CO_2H\\CO>O\end{cases}$, melting at 149°, and beyond 180° decomposing into carbon dioxide and phthalide. It is formed by the reduction of o-carbo-phenyl-glyoxylic acid (B. **18,** 381; **31,** 373), or by boiling the ω-dibromo-aceto-phenone-o-carboxylic acid $HO_2CC_6H_4COCHBr_2$, m.p. 132°, with water (B. **40,** 71), as well as by the action of alkali upon tetrachloro-hydrindone (A. **334,** 341). Substituted phthalide-carboxylic acids, see A. **296,** 344.

Acetonyl-phthalide $C_6H_4\begin{cases}CH—CH_2COCH_3\\CO>O\end{cases}$, m.p. 68°, from acetone with phthal-aldehydic acid (C. 1898, II. 980).

Phthalide-acetic acid $C_6H_4\begin{cases}CH.CH_2.CO_2H\\CO>O\end{cases}$, melting at 150°, is derived from phthalyl-acetic acid by reduction (B. **10,** 1558, 2200).

Meconin-acetic acid $(HO)_2[5,6]C_6H_2\begin{cases}[1]CH—CH_2.CO_2H\\[2]CO>O\end{cases}$, melting at 228°, results from the action of hydriodic acid upon **meconin-acetic acid** $(CH_3O)_2[5,6]C_6H_2\begin{cases}[1]CH.CH_2.CO_2H\\[2]CO>O\end{cases}$. The latter is formed in the condensation of opianic acid with malonic acid, glacial acetic acid, and sodium acetate (B. **19,** 2295).

Dihydro-iso-cumarin-carboxylic acid $C_6H_4\begin{cases}[1]CH_2.CH.CO_2H\\[2]CO—O\end{cases}$, melting at 153°, is isomeric with phthalide-acetic acid. It is produced in the oxidation of dihydro-naphthol (see this) with potassium permanganate (B. **26,** 1841).

Phthalide-propionic acid $C_6H_4\begin{cases}[1]CH—CH_2.CH_2CO_2H\\[2]CO\end{cases}>O$, melting at 140°, results from the reduction of phthalyl-propionic acid (B. **11**, 1681).

o-Phenylene-aceto-glycol-lactone acid $C_6H_4\begin{cases}[1]CH(CO_2H)O\\[2]CH_2——CO\end{cases}+1\frac{1}{2}H_2O$, m.p. 85°, is obtained from phenylene-diacetic acid, bromine, phosphorus, and water (B. **26**, 223).

o-Carbo-phenyl-glyceric acid lactone $C_6H_4\begin{cases}[1]CH(OH).CH.CO_2H\\[2]CO——O\end{cases}$, m.p. 202°, is produced when β-naphtho-quinone is oxidised with a bleaching-lime solution. When the lactone acid is heated with hydrochloric acid it loses water and becomes o-carbon-α-oxy-cinnamic acid lactone (B. **27**, 198).

(19) Phenylene-ketone-dicarboxylic Acids.

o-Carbo-phenyl-glyoxylic acid, *phthalonic acid* $C_6H_4\begin{cases}[1]CO.CO_2H\\[2]CO_2H\end{cases}$, m.p. 138°–140°, is formed in the oxidation of o-hydrindene-carboxylic acid (*q.v.*), naphthalene, α-naphthol, β-naphthol, and the oxy-quinone of β-phenyl-naphthalene with potassium permanganate (A. **240**, 142; B. **31**, 369). It yields o-carbo-mandelic acid upon reduction, and also homo-phthalic acid. Heating the acid alone gives phthalic anhydride, phthal-aldehydic acid, and biphthalyl. Ester and ester acids, see C. 1904, I. 514.

Trichloro-aceto-benzoic acid $C_6H_4\begin{cases}[1]CO.CCl_3\\[2]CO_2H\end{cases}$, m.p. 144°, and **tribromo-aceto-benzoic acid,** m.p. 160°, result when chlorine or bromine, in glacial acetic acid, acts upon phthalyl-acetic acid (B. **10**, 1556).

o-Carbo-benzoyl-acetic acid $C_6H_4\begin{cases}[1]CO.CH_2.CO_2H\\[2]CO_2H\end{cases}$, m.p. 90° with decomposition into carbon dioxide and aceto-phenone-o-carboxylic acid, is formed when phthalyl-acetic acid is dissolved in an excess of caustic soda and precipitated with acids (B. **10**, 1553).

ω-Cyano-aceto-phenone-o-carboxylic acid melts at 136° (B. **26**, R. 371).

Benzoyl-cyano-aceto-ester-o-carboxylic acid $CO_2H[2]C_6H_4.CO.CH\begin{cases}CO_2C_2H_5\\CN\end{cases}$, m.p. 121°, is produced by the action of soda upon phthalyl-cyano-acetic ester (B. **26**, R. 370).

o-Carbo-benzoyl-propionic acid $C_6H_4\begin{cases}[1]CO.CH_2.CH_2.CO_2H\\[2]CO_2H\end{cases}$, m.p. 137°. The *double lactone* $C_6H_4\begin{cases}C\begin{cases}——CH_2.CH_2.CO\\CO\end{cases}O\end{cases}$, corresponding to this acid, is produced on heating succinic anhydride and phthalic anhydride with sodium acetate (B. **11**, 1680; **18**, 3119).

(20) Tri- and Tetracarboxylic Acids.

Benzyl-malonic-o-carboxylic acid, *o-carbo-benzyl-malonic acid* $C_6H_4\begin{cases}CH_2.CH(CO_2H)_2\\CO_2H\end{cases}$, breaks down at 190° into hydro-cinnamic-o-

carboxylic acid and CO_2. Its diethyl ester results from the reduction of phthalyl-malonic ester (A. **242**, 37).

o-, m-, and **p-Xylylene-dimalonic tetra-ethyl esters** $C_6H_4[CH_2.CH(CO_2C_2H_5)_2]_2$ are produced in the reduction of the three corresponding **xylylene-dichloro-dimalonic esters** $C_6H_4[CH_2CCl(CO_2C_2H_5)_2]_2$, which are the products of the action of sodium chloro-malonic ester upon the ω-xylylene dibromides (B. **21**, 31). The xylylene-dimalonic acids break down, on heating, into phenylene-dipropionic acids and $2CO_2$.

m-Xylylene-diaceto-acetic ester $C_6H_4[1,3][CH_2.CH(COCH_3)CO_2R]_2$ from m-xylylene bromide and Na-aceto-acetic ester (B. **34**, 2790).

(21) Oxy-tri-, tetra-, and pentacarboxylic Acids.

Phthalyl-diacetic acid $C_6H_4\begin{cases}C[CH_2.CO_2H]_2\\ \diagdown\!\diagup\\ COO\end{cases}$, m.p. 158°, is obtained from **phthalyl-dimalonic acid** $C_6H_4\begin{cases}C(CH)(CO_2H)_2\\ \diagdown\!\diagup\\ COO\end{cases}$ (A. **242**, 80).

Phthalide-tricarboxylic acid $(COOH)_2C_6H_2\begin{cases}CH{-}COOH\\ CO\!>\!O\end{cases}$, by condensation of pyro-racemic acid and *diacetyl-glyoxylic acid* $(CH_3COO)_2CH.COOH$ with alkalies. On boiling with water the acid loses CO_2, and passes into phthalide-dicarboxylic acid $(CO_2H)_2C_6H_2\langle\begin{matrix}CH_2\\ CO\end{matrix}\rangle O$, which, on oxidation, yields *prehnitic acid* (A. **311**, 132).

(22) Ketone-tricarboxylic Acids.

2, 6-Dicarbo-phenyl-glyoxylic acid $(CO_2H)_2[2,6]C_6H_3CO.CO_2H$, melting at 238°, is formed when naphthalic acid is oxidised with $KMnO_4$ (B. **26**, 1798). Hydriodic acid and phosphorus reduce it to 2-methyl-iso-phthalic acid, and when heated it becomes 2-aldehydo-iso-phthalic acid, while more complete oxidation converts it into hemi-mellitic acid (B. **29**, R. 282).

Iregenone-di- and tri-carboxylic acids $CH_3[4]C_6H_2\begin{cases}[1]C(CH_3)_2CO_2H\\ [2]CO.CO_2H\end{cases}$ and $CO_2H[4]C_6H_2\begin{cases}[1]C(CH_3)_2CO_2H\\ [2]CO.CO_2H\end{cases}$ (B. **26**, 2684).

Mono-nuclear, Aromatic Substances, with Unsaturated Side Chains.

The benzene derivatives thus far considered contain saturated side chains having carbon present in them. To these are attached the compounds having *unsaturated side chains—e.g.* :

Phenyl-ethylene, Styrol	$C_6H_5.CH:CH_2$	Phenyl Acetylene	$C_6H_5C:CH$
Cinnamyl Alcohol, Styrone	$C_6H_5.CH:CH.CH_2OH$	Phenyl Acetylene Alcohol	$C_6H_5C:C.CH_2OH$
Cinnamyl Aldehyde	$C_6H_5.CH:CH.CHO$	Phenyl Acetylene Aldehyde	$C_6H_5C:C.CHO$
Cinnamic Acid	$C_6H_5.CH:CH.CO_2H$	Phenyl Propiolic Acid	$C_6H_5C:C.CO_2H$.

They can, like the unsaturated aliphatic bodies, be converted by numerous additive reactions into saturated compounds, as has frequently been shown in the preceding sections.

I*a*. Olefin-benzenes.

For the preparation of the olefin-benzols containing the olefin linkage in the neighbourhood of the benzene nucleus, the secondary

and tertiary phenyl-alkyl-carbinols are particularly suited, and can be easily prepared from the synthetic acidyl-benzols by reduction or by the action of magnesium alkyl-iodides.

These carbinols are (1) made into chlorides by treatment with HCl at 0°, and HCl is split off from the latter by heating with pyridin :

$$C_6H_5COCH_3 \longrightarrow C_6H_5CH(OH)CH_3 \longrightarrow C_6H_5CHClCH_3 \longrightarrow C_6H_5CH:CH_2.$$

(2) The addition products obtained from acidyl-benzols or benzol-carboxylic esters split up on heating with excess of AlkMgI (B. **35,** 2633, 3506) :

$$C_6H_5COCH_3 \longrightarrow C_6H_5C\begin{matrix}\diagup\!\!\diagdown (CH_3)_2 \\ \diagdown\!\!\diagup OMgI\end{matrix} \longrightarrow C_6H_5C\begin{matrix}\diagup\!\!\diagdown CH_2 \\ \diagdown\!\!\diagup CH_3\end{matrix}.$$

According to the position of the ethylene double linking to the benzene nucleus we distinguish Δ^1, Δ^2, and Δ^3 olefin-benzols or styrols, differing in density, boiling-point, molecular refraction, and heat of combustion (B. **36,** 1628, 3584 ; **37,** 2301 ; A. **373,** 288).

On heating with alcoholic potash, the Δ^2-styrols are converted into the isomeric Δ^1-styrols. This is reversible to some extent (C. 1905, II. 1017).

Styrol, phenyl-ethylene, *vinyl-benzol* $C_6H_5.CH:CH_2$, boiling at 144°, occurs in storax (1–5 per cent.), from which it is obtained upon distillation with water. It also accompanies crude xylene in coal-tar (B. **23,** 3169, 3269). It is prepared (1) from chlorethyl-benzol by heating with pyridin to 130° (B. **36,** 1632) ; (2) from β-bromo-hydrocinnamic acid, heated in NaHO, when it splits up cleanly into CO_2, BrH, and styrol ; (3) by heating cinnamic acid with lime (B. **23,** 3269) or water to 200° ; (4) from phenyl-acetylene by partial reduction with zinc and glacial acetic acid or Na and methyl alcohol ; (5) by the condensation of acetylene, C_2H_2, upon application of heat. (6) From vinyl bromide, benzene, and aluminium chloride (A. **235,** 331). (7) It is best obtained from β-bromo-hydro-cinnamic acid, which is immediately decomposed by a soda solution into styrol, carbon dioxide, and hydrobromic acid. It is a mobile, strongly refracting liquid, with an agreeable odour. Pure styrolene is optically inactive ; its sp. gr. = 0·925 at 0°.

Hydriodic acid converts styrolene into ethyl-benzene $C_6H_5C_2H_5$; hydrochloric and hydrobromic acids change it to α-haloid ethyl-benzenes (B. **26,** 1709), while with chlorine and bromine it yields α,β-di-haloid ethyl-benzenes ; chromic acid or nitric acid oxidises it to benzoic acid.

With xylene and sulphuric acid, styrol forms β-phenyl-α-tolyl-propane ; and with phenol, oxy-diphenyl-ethane (B. **24,** 3889). Nitrous acid converts it into **styrol-pseudo-nitrosites** $C_6H_5.C_2H_3.(N_2O_3)$ (B. **29,** 356). It is polymerised to meta-styrol (C_8H_8) on standing, or in sunlight, whence styrol is regenerated by distillation (C. 1899, II, 1117 ; A. **371,** 259).

A. *Styrols substituted in the Side Chains.*—Two series of mono-substituted styrols result from the replacement of vinyl-hydrogen. They are known as α- and ω-substituted products :

α-Bromo-styrol $C_6H_5Br:CH_2$.
ω-Bromo-styrol $C_6H_5.CH.CHBr$.

The *α-products* result on heating styrol chloride (bromide) alone, with lime, or with alcoholic potash. They possess a penetrating odour, causing tears. They yield aceto-phenone (B. **14,** 323) when they are heated with water (to 180°) or with sulphuric acid. *α-Chloro-styro* also results from aceto-phenone chloride when it is digested with alcoholic potash.

α-Chloro-styrol	boils at	190°.
α-Bromo-styrol	,,	150°–160° (75 mm.).
ω-Chloro-styrol	,,	199°.
ω-Bromo-styrol	,,	108° (20 mm.).

The *ω-products* are derived (along with phenyl-acetaldehyde) from the β-phenyl-α-chloro- (bromo-) lactic acids, upon heating with water. **ω-Chloro-styrol** is obtained also from ω-dichloro-ethyl-benzol with alcoholic potash. **ω-Bromo-styrol** is formed from dibromo-hydro-cinnamic acid by boiling with water. When they are heated with water, phenyl-acetaldehyde results. They are oils having a hyacinth-like odour.

See, further, Phenyl-acetylene and Phenyl-propiolic acid.

Sym. dichloro-styrol $C_6H_5.CCl : CHCl$ boils at 221° (B. **10,** 533), from phenyl-acyl chloride with PCl_5; gives diphenyl-pyrazin on heating with ammonia (B. **33,** 2654; **35,** 2294).

Dibromo-styrol boils at 253° (B. **17,** R. 22).

Di-iodo-styrol, *phenyl-acetylene di-iodide,* m.p. 76°, is obtained from phenyl-acetylene and iodine (B. **26,** R. 18). **Tri-iodo-styrol,** *phenyl-tri-iodo-ethylene* $C_6H_5.CI : CI_2$, m.p. 108°, is obtained from phenyl-iodo-acetylene and iodine dissolved in CS_2 (B. **26,** R. 19).

Unsym. dichloro-styrol $C_6H_5CH : CCl_2$, b.p. 225°, is found among the products of the reaction of chloral upon benzene in presence of ACl_3 (A. **296,** 263; C. 1900, II. 326). **Trichloro-styrol** $C_6H_5CCl : CCl_2$, b.p. 235°.

ω-Nitro-styrols generally result from the condensation of benzaldehydes and nitro-methane by means of sodium ethylate or aliphatic amines (B. **37,** 4502); in the former case there are intermediate products in the shape of sodium salts of nitro-alcohols $C_6H_5CH(OH)CH : NOONa$, which easily split off H_2O and become ω-nitro-styrols. On reduction with Al amalgam or zinc dust and acetic acid the nitro-styrols form **aryl-acetaldoximes** $C_6H_5CH_2.CH : NOH$ (C. 1902, II. 449).

ω-Nitro-styrol, *phenyl-nitro-ethylene* $C_6H_5.CH : CH(NO_2)$, m.p. 58°, is obtained by boiling styrol with fuming nitric acid, by condensation of benzaldehyde with nitro-methane $CH_3(NO_2)$ (B. **31,** 656; **32,** 1293; A. **325,** 7), as well as by the action of fuming nitric acid upon phenyl-iso-crotonic acid (B. **17,** 413), or by the action of NO_2 upon cinnamic acid, when the dinitro-compound $C_6H_5.C_2H_2(NO_2)_2.CO_2H$, formed at first, decomposes (B. **18,** 2438; **29,** 357). It possesses a peculiar odour, provoking tears, is readily volatilised in aqueous vapour, and forms yellow needles. Dilute sulphuric acid decomposes it into benzaldehyde, carbon monoxide, and hydroxylamine. It combines with sodium methylate, or ethylate, to form sodium salts $C_6H_5CH(OR).CH : NOONa$, from which CO_2 separates out phenyl-methoxy- and ethoxy-nitro-ethane in the form of yellowish oils, boiling at 136° and 137° (12 mm.) (B. **38,** 466). **p-Phenylene-bis-nitro-ethylene** $C_6H_4(CH_2CH.NO_2)_2$ is obtained from terephthalic aldehyde with nitro-methane (B. **32,** 1295).

Phenyl-vinyl-amine, *ω-amido-styrol* $C_6H_5.CH:CHNH_2$, is very unstable. It is obtained by heating α-amido-cinnamic acid (B. **17,** 1622), and from ω-nitro-styrol (B. **26,** R. 677).

B. *Styrols substituted in the Benzene Nucleus.*—The three nitro-styrols are produced by the action of a cold soda solution upon the nitro-phenyl-bromo-lactic acids, or by boiling the β-lactones of the phenyl-bromo-lactic acids with water (B. **16,** 2213; **17,** 595).

o-, m-, and **p-Nitro-styrols** $NO_2C_6H_4CH:CH_2$ melt at +13°, −5°, and +29°. **o-Amido-styrol** is a very unstable, oily body. **m-Amido-styrol,** b.p. 112°–115° (12 mm.), is an oil which polymerises with ease. **m-Azo-styrol** melts at 38° (B. **26,** R. 677). **p-Amido-styrol,** m.p. 81°, is formed on heating p-amido-cinnamic acid, and, together with p-amido-cinnamic acid, in the reduction of p-nitro-cinnamic ester (B. **15,** 1984).

C. *Styrols substituted both in the benzene nucleus and in the side chain* PCl_5 convert o- and p-nitro-aceto-phenones into liquid ortho- and **p-nitro-α-chloro-styrol** $NO_2.C_6H_4.CCl:CH_2$, melting at 63° (A. **221,** 329).

o-Nitro-ω-chloro-styrol $NO_2.C_6H_4.CH:CHCl$, melting at 58°, is obtained from o-nitro-cinnamic acid and hypochlorous acid (B. **17,** 1070).

o-Amido-chloro-styrol, melting at 56°, yields indol when it is heated to 170° with sodium alcoholate; see also o-oxy-ω-chloro-styrol. **o-, m-,** and **p, ω-Dinitro-styrol** melt at 107°, 125°, and 199° respectively, with decomposition; see B. **31,** 657, 1294; C. 1902, II. 449.

D. *Homologous Olefin-benzols.*—**m-** and **p-Methyl-styrol,** *vinyl-toluols* $CH_3C_6H_4CH:CH_2$, b.p. 164° and b.p. 60°; **4-ethyl-styrol,** $b.p._{20}$ 86°; **2, 4, 5-** and **2, 4, 6-trimethyl-styrol,** m.p. 118°, b.p. 213° and $b.p._{14}$ 92° have been prepared mostly by method 1 (B. **24,** 1332; **31,** 1007; **35,** 2245). For other olefins of the mesitylene series, dimethyl-styrols, see B. **37,** 924.

Propenyl-benzol, *iso-allyl-benzol* $C_6H_5.CH:CHCH_3$, $b.p._{13}$ 74°, from α-chloro-propyl-benzol with pyridin, from cinnamic alcohol by reduction with HI, from ω-bromo-styrol with CH_3MgI, and from **α, β-chloro-bromo-propenyl-benzol** $C_6H_5CCl:CBrCH_3$, a transformation product of bromo-propionyl-benzol $C_6H_5.COCHBrCH_3$, by reduction with sodium in ether (B. **36,** 3033).

Allyl-benzol $C_6H_5.CH_2.CH:CH_2$, b.p. 155°, from benzene-allyl iodide and zinc dust (A. **172,** 132) or from C_6H_5MgBr and allyl bromide (C. 1904, II, 1038).

Iso-propenyl-benzol, *metho-vinyl-benzol* $C_6H_5C(CH_3):CH_2$, b.p. 162°, from aceto-phenone or benzoic acid ester with excess of magnesium-methyl iodide, or from $C_6H_5C(CH_3)_2OMgI$ with NH_3; similarly, **metho-propenyl-, metho-butenyl-,** and **metho-hexenyl-benzols** have been prepared, boiling at 192°, 199°, and 210° (20 mm.) respectively. On the elimination of formaldehyde from metho-vinyl-benzol by atmospheric oxidation, see C. 1902, II. 1505. Optically active **metho-pentenyl-benzol,** $b.p._9$ 100°–103°, $[\alpha]_D$ 50·3° (B. **37,** 653). **ω-Bromiso-propenyl-benzol** $C_6H_5C(CH_3):CHBr$, $b.p._9$ 106°, from dibromo-β-methyl-cinnamic acid with NaHO. With alcoholic potash and migration of the phenyl group it yields phenyl-alkylene (C. 1907, I. 1201).

Δ^2-Butenyl-benzol $C_6H_5CH_2CH:CHCH_3$, b.p. 176°, D_{15} 0·8857,

n_D 1·5109, from benzyl-acetone by reduction and dehydration, or by reduction of phenyl-butadiëne with sodium and alcohol. On heating to 180° with alcoholic potash it passes into the isomeric **Δ^1-butenyl-benzol** $C_6H_5CH : CH.CH_2.CH_3$, b.p. 189°, D_{16} 0·9124, n_D 1·5414, which also results from benzaldehyde treated with propyl-magnesium iodide, and which is reduced by nitrogen and alcohol to n-butyl-benzol, in contrast with Δ^2-butenyl-benzol (B. **37,** 2310).

Δ^1-Iso-amenyl-benzol $C_6H_5CH : CH.CH(CH_3)_2$, b.p. 207°. **Δ^2-Iso-amenyl-benzol** $C_6H_5CH_2.CH : C(CH_3)_2$, b.p. 205° (B. **37,** 2314).

I*b*. Acetylene Benzenes.

Phenyl-acetylene, *acetenyl-benzene,* $C_6H_5.C : CH$, boiling at 139°, is produced (1) when α-bromo-styrolene and (2) aceto-phenone chloride are heated to 130° with alcoholic potash; (3) also from phenyl-propiolic acid, on heating it with water to 120°, or upon distilling the barium or aniline salt (B. **29,** R. 797), or the copper salt with steam (A. **342,** 222). Phenyl-acetylene is a liquid with an agreeable odour. Like acetylene, it forms a compound with ammoniacal silver solution and with a solution of cuprous chloride, **phenyl-acetylene-silver** $C_6H_5.CCAg$, white (B. **25,** 1096), and **phenyl-acetylene-copper** $C_6H_5.C : C.Cu$, light yellow, which dissolves in glacial acetic acid with an orange coloration and formation of the very oxidisable double salt $C_6H_5C : C.Cu$, CH_3COOCu, and of diphenyl-butenin (A. **342,** 193). **Phenyl-acetylene-sodium** $C_6H_5C : CNa$ is formed by the action of sodium upon an ether solution of phenyl-acetylene; it condenses with aldehydes and ketones to phenyl-acetylene alcohols, with formic ester to phenyl-acetylene-aldehyde, with homologous acid esters or chlorides to phenyl-acetylene-ketones, with chloro-carbonic ester to phenyl-propiolic ester, and with CO_2 to phenyl-propiolic acid. Treated with hydrated sulphuric acid, phenyl-acetylene becomes aceto-phenone, and by boiling with acetic acid or alcohol, and zinc dust, it becomes styrol, with small quantities of diphenyl-butadiëne (B. **22,** 1184).

Phenyl-chloro-acetylene $C_6H_5C : CCl$, $b.p._{14}$ 74°. **Phenyl-bromo-acetylene** $C_6H_5C : CBr$, $b.p._{15}$ 96°. **Phenyl-iodo-acetylene** $C_6H_5C : CI$, $b.p._{22}$ 136°, are converted by sulphuric acid into the corresponding phenacyl haloids (B. **26,** R. 20; A. **308,** 292). Various aryl-chloro-acetylenes are formed from the corresponding α, β-dichloro-styrols with alcoholic potash, while metallic sodium forms aryl-acetylenes (B. **33,** 2654, 3261).

o-Nitro-phenyl-acetylene and **p-nitro-phenyl-acetylene** $C_6H_4\langle^{C : CH}_{NO_2}$, melting at 81°–82° and 152°, are produced on boiling o- and p-nitro-phenyl-propiolic acid with water.

o-Amido-phenyl-acetylene $C_6H_4(NH_2)C : CH$ is an oil with an odour resembling that of the indigo vat. It is produced in the reduction of o-nitro-phenyl-acetylene with zinc dust and ammonia, or with ferrous sulphate and potassium hydroxide, and in the decomposition of o-amido-phenyl-propiolic acid.

Phenyl-methyl-acetylene, *phenyl-allylene* $C_6H_5.C : C.CH_3$, boiling at 185°, is produced on boiling phenyl-bromo-propylene with alcoholic potash (B. **21,** 276). **Phenyl-ethyl-acetylene,** boiling at 201°, is

obtained from sodium phenyl-acetylide and ethyl iodide, as well as from phenyl-iodo-acetylene and zinc ethide.

Ic. Diolefin-benzols.

A. **p-Divinyl-benzol** $C_6H_4(CH : CH_2)_2$ is a liquid with an odour like that of petroleum. It is produced when p-di-α-bromo-ethyl-benzol is heated with quinolin (B. **27,** 2528).

B. **Phenyl-butadiëne** $C_6H_5CH : CH.CH : CH_2$, m.p. −3·5°, b.p.$_{18}$ 95°, is formed by the action of excess of methyl-magnesium iodide upon cinnamic aldehyde (B. **37,** 2310), from cinnamylidene malonic or acetic acid by splitting off CO_2; also from the chloride of styryl-methyl-carbinol $C_6H_5CH : CH.CHCl.CH_3$ by boiling with pyridin. It polymerises on standing, and does so rapidly on heating to 150°, forming bimolecular bis-diphenyl-butadiëne $(C_{10}H_{10})_2$, b.p.$_{17}$ 221° (B. **37,** 2272). Sodium and alcohol reduce phenyl-butadiëne to **Δ²-butenyl-benzol.** With bromine it forms a **1, 4-dibromide** $C_6H_5CHBrCH : CH.CH_2Br$, m.p. 94°, and with $2Br_2$ a **tetrabromide** $C_6H_5CHBrCHBr.CHBrCH_2Br$. The dibromide changes with zinc methyl and ethyl into **dimethyl** and **diethyl-butenyl-benzol** $C_6H_5CH(Alk)CH : CHCH_2(Alk)$. With diazo-acetic ester, phenyl-butadiëne combines to form **styryl-trimethylene-carboxylic ester** $C_6H_5CH : CH.CH\langle^{CH.CO_2R}_{CH_2}$ (B. **37,** 2101).

An isomeric (?)-phenyl-butadiëne and its polymerisation product are formed from cinnamenyl-acrylic acid (cinnamylidene-acetic acid) by heating with barium hydroxide (B. **35,** 2649, 2696; **36,** 1404).

Phenyl-methyl-butadiëne $C_6H_5CH : CH.C(CH_3) : CH_2$, b.p.$_{32}$ 124°, and **phenyl-methyl-pentadiëne** $C_6H_5CH : CH.C(CH_3) : CHCH_3$, b.p.$_{21}$ 133°, from benzal-acetone, with magnesium methyl and ethyl iodide by method 2 (B. **35,** 2651). **Phenyl-pentadiëne** $C_6H_5CH : CH.CH : CH.CH_3$, b.p.$_{16}$ 116°. **Phenyl-hexadiëne** $C_6H_5CH : CH.CH : CH.CH_2CH_3$, b.p.$_{16}$ 128°, from cinnamic aldehyde and ethyl- or propyl-magnesium iodide respectively (B. **40,** 1768).

Trimethyl-phenyl-allene $C_6H_5(CH_3)C : C : C(CH_3)_2$, b.p.$_{20}$ 108°, a strongly refractive liquid with an odour resembling lemon, is formed by the action of C_6H_5MgBr upon mesityl oxide. On oxidation with KMnO it yields aceto-phenone, and on reduction with Na and alcohol Δ²-hexenyl-benzol (B. **37,** 2305).

Id. Olefin-acetylene-benzols, like **iso-propenyl-phenyl-acetylene** $C_6H_5C \vdots C.C(CH_3) : CH_2$, b.p.$_7$ 88°, and **iso-butenyl-phenyl-acetylene** $C_6H_5C \vdots C.C(CH_3) : CH.CH_3$, b.p.$_9$ 103°, have been prepared from phenyl-acetylene alcohols, by splitting off water with sulphuric acid or potassium bisulphate (C. 1905, II. 1018).

IIa. Olefin-phenols.

Various representatives of this class occur in the vegetable kingdom: chavicol, chavibetol, estragol, anethol, eugenol, safrol, asarone, apiol, etc. All are phenol-like derivatives of *allyl-* and iso-allyl- or *propenyl-benzene.* The *allyl* fatty derivatives occurring in the vegetable kingdom were *mustard oil* (I. 423) and *oil of garlic* (I. 150).

A. **Olefin-monoxy-benzols.**—**o-Vinyl-phenol** $CH_2 : CH.C_6H_4OH$, m.p. 29, b.p.$_{15}$ 108°, smells like phenol, and is formed by slow distillation of o-cumaric acid in a vacuum (B. **41,** 367).

m-Vinyl-phenol $CH_2 : CH.C_6H_4.OH$, b.p. 115° (16 mm.), is obtained from m-amido-styrol. **o-, m-,** and **p-vinyl-anisols** $CH_2 : CH.C_6H_4.O.CH_3$ boiling at 83° (11 mm.), 90° (14 mm.), and 91° (13 mm.) respectively, are easily polymerised oils, obtained from the corresponding methoxy-aceto-phenones by method 1 ; the o- and p-derivatives have also been obtained from the methoxy-cinnamic acids (B. **11,** 515 ; **36,** 3587).

o-Oxy-ω-chloro-styrol $HO[2]C_6H_4.CH : CHCl$, m.p. 54°, is obtained from o-amido-ω-chloro-styrol. Caustic potash converts it into cumarone (*q.v.*). **o-Thio-ω-chloro-styrol** $HS.C_6H_4.CH : CHCl$, see Benzothiophene.

Allyl- and Propenyl-phenols.—A very common property of the allyl-phenols is their rearrangement, induced by hot alcoholic potash, into isomeric-propenyl compounds :

Methyl-chavicol	$CH_3O.C_6H_4.CH_2.CH : CH_2 \longrightarrow CH_3O.C_6H_4.CH : CH.CH_3$	Anethol.
Methyl-eugenol	$(CH_3O)_2C_6H_3.CH_2.CH : CH_2 \longrightarrow (CH_3O)_2C_6H_3.CH : CH.CH_3$	Methyl-iso-eugenol.
Safrol	$(CH_2O_2)C_6H_3.CH_2.CH : CH_2 \longrightarrow (CH_2O_2)C_6H_3.CH : CH.CH_3$	Iso-safrol.
Apiol	$\left.\begin{matrix}(CH_3O)_2\\(CH_2O_2)\end{matrix}\right\}C_6H.CH_2.CH : CH_2 \rightarrow \left.\begin{matrix}(CH_3O)_2\\(CH_2O_2)\end{matrix}\right\}C_6H.CH : CH.CH_3$	Iso-apiol.

The propenyl derivatives are distinguished from their allyl derivatives by higher specific gravities, higher melting-points, and greater refractive power (B. **22,** 2747 ; **23,** 862). When the propenyl compounds are acted upon by nitrous acid, in glacial acetic acid, they yield *di-iso-nitroso-peroxides,* derivatives of α-diketones (see Anethol). The allyl- and propenyl-phenols, when carefully oxidised with potassium permanganate, yield *phenol-glycols* and *phenol-glyoxylic acids* ; and, on oxidation with ozone, oxy-benzaldehydes and oxy-phenyl-acet-aldehydes (B. **41,** 2751). Mercuric acetate oxidises the propenyl compounds to glycols, with elimination of mercuric acetate. The allyl bodies form only addition products, from which the allyl-phenols can be regenerated by decomposition with acids or by reduction (B. **36,** 3577 ; C. 1906, II. 119 ; B. **42,** 1502). By boiling with concentrated formic acid the propenyl compounds are resinified, while the allyl compounds remain unchanged (B. **41,** 2185). The iodo-hydrins of the propenyl compounds, on treatment with $AgNO_3$ or HgO, form aldehydes, with migration of the aromatic residue. Thus anethol forms *p-methoxy-hydratropic aldehyde* $CH_3OC_6H_4CH(CH_3)CHO$. In the dibromides of the propenyl compounds the bromine atom adjoining the phenyl group is easily movable ; they can therefore be converted into ketones by treatment with two molecules sodium methylate, *e.g.* anethol dibromide into anisoyl-ethyl-ketone. This cannot be done in the case of the allyl dibromides.

Chavicol, *p-allyl-phenol* $CH_2 : CH.CH_2[4]C_6H_4OH$, b.p. 237°, occurs in the oil obtained from the leaves of *Chavica Betle.* Also in betel oil and ethereal bay oil. It is a colourless oil, with peculiar odour, and its aqueous solution is coloured blue by a drop of ferric chloride. *Methyl-chavicol* boils at 226°, and *ethyl-chavicol* boils at 232° (B. **23,** 862).

Estragol, methyl-chavicol, occurs in tarragon oil and other ethereal

oils (B. **27**, R. 46). It boils at 215° (compare B. **27**, R. 46; **29**, 544; C. 1899, I. 1196). Synthetically it is formed by the action of allyl bromide upon p-methoxy-phenyl-magnesium bromide (C. 1904, II. 1038). It changes into anethol when heated with alcoholic potash.

p-Anol, *p-propenyl-phenol* $CH_3.CH : CH[4]C_6H_4OH$, m.p. 92°, is prepared by heating anethol with caustic alkali (A. Suppl. **8**, 88); or, synthetically, from p-oxy-benzaldehyde and excess of ethyl-magnesium bromide (C. 1908, I. 1624).

Anethol, *p-propenyl-anisol* $CH_3.CH : CH[4]C_6H_4.O.CH_3$, m.p. 21°, and b.p. 232°, occurs in anise oil, from the seed of *Pimpinella anisum*, in that from the seed of *Illicium anisatum*, in the fruit of *Anethum fæniculum*, and in fennel and tarragon oils. It is also formed from methyl-chavicol (see above). It has been obtained synthetically from ethyl Mg iodide and anisaldehyde (B. **37**, 4188) and from β-p-methoxy-phenyl-methacrylic acid by heating; this would prove that its constitution is that of p-propenyl-anisol (B. **10**, 1604). Chromic acid oxidises it to anisic and acetic acids, while dilute nitric acid changes it to anisic aldehyde. Methoxy-phenyl-glyoxylic acid is produced on treating it with potassium permanganate; anisyl-propenyl-glycol on treating it with mercuric acetate; and methoxy-hydratropic aldehyde by treatment with iodine and mercuric oxide. With HNO_2 it unites according to the conditions either to form **anethol-pseudo-nitrosite,** *anethol nitrite* $CH_3OC_6H_4CH(NO).CH(NO_2)CH_3$, m.p. 121°, or p-methoxy-phenyl-methyl-glyoxime $CH_3OC_6H_4C(NOH)C(NOH)CH_3$, or its peroxide. The anethol nitrite splits off hyponitrous acid on treatment with acetyl chloride or sodium methylate, and becomes **β-nitro-anethol** $CH_3OC_6H_4CH : CH[NO_2].CH_3$, m.p. 47°, yellow needles.

Anethol-nitroso-chloride $CH_3OC_6H_4CHCl.CH(NO).CH_3$, m.p. 128° (A. **332**, 318). **o-** and **m-Propenyl-anisol,** b.p. 220° and 227° (B. **29**, R. 644; **36**, 1188).

o-, m-, and **p-iso-propenyl-anisols** boil at 199°, 215°, and 222° respectively. They are formed from the anisol-carboxylic esters with CH_3MgI (C. 1904, II. 593; 1908, I. 1624; II. 595). Like the propenyl compounds, the iso-propenyl compounds are easily reduced with Na and alcohol. On oxidation with $KMnO_4$ oxy-aceto-phenones are generated. Treated with $AgNO_3$ their iodo-hydrins yield ketones, with migration of the aromatic residue.

B. **Olefin-dioxy-benzols.**—Of this group it is the olefin-3, 4-dioxy-benzols which are almost exclusively known. They usually occur, as ethers, in plants, or are obtained by the breaking down of plant acids.

Free **vinyl-pyro-catechin** $(HO)_2[3, 4]C_6H_2CH : CH_2$ seems to be unstable and easily polymerised. Its carbonate $CO(O_2)C_6H_3CH : CH_2$, m.p. 66°, is formed by the dry distillation of 3, 4-dioxy-benzal-malonic carbonate (B. **41**, 4153).

Hesperetol, *vinyl-3, 4-guaiacol* $\left.\begin{matrix}HO[3]\\CH_3O[4]\end{matrix}\right\}C_6H_3.CH : CH_2$, m.p. 57°, is produced in the dry distillation of calcium iso-ferulate (B. **14**, 967).

Vinyl-3,4-pyro-catechin-methylene ether $CH_2\left\langle\begin{matrix}O\\O\end{matrix}\right\rangle C_6H_3CH : CH_2$, b.p.$_{15}$ 108°, from piperonal and magnesium-methyl iodide (B. **36**, 3595).

Allyl-3, 4-pyro-catechin $(HO)_2[3, 4]C_6H_3CH_2.CH : CH_2$, m.p. 49°, b.p.$_4$ 139°, has been found in the oil of Java betel leaves. It possesses

a feeble odour, recalling creosote; its alcoholic solution is coloured deep green by ferric chloride (C. 1907, II. 1741). More frequently the ethers of allyl-pyro-catechin are found among the ethereal oils. Of these substances, special mention should be made of eugenol and safrol, the foundation materials for the artificial production of the perfumes vanillin and heliotropin.

Eugenol, *allyl*-4, 3-*guaiacol, eugenic acid, carnation acid* $\left.\begin{matrix}HO[4]\\CH_3O[3]\end{matrix}\right\}C_6H_3.CH_2.CH:CH_2$, is an aromatic oil, boiling at 247°. It is coloured blue by ferric chloride: It occurs in the oil from *Eugenia caryophyllata*, in that from *Eugenia pimenta*, etc. Sodium amalgam reduces coniferyl alcohol to eugenol (B. **9,** 418). Potassium permanganate oxidises it to vanillin and vanillinic acid. Heated with excess of alcoholic potash, it is transposed into the isomeric iso-eugenol. See B. **27,** 2455; **28,** 2082, for the derivatives of eugenol.

Chavibetol, *betel-phenol, allyl*-3, 4-*guaiacol* $\left.\begin{matrix}HO[3]\\CH_3O[4]\end{matrix}\right\}C_6H_3.CH_2.CH:CH_2$, boiling at 254°, occurs in the ethereal oil obtained from the leaves of *Piper Betle* (*J. pr. Ch.* 2, **39,** 349; B. **23,** 862).

Eugenol-methyl ether, *allyl*-3, 4-*veratrol* $(CH_3O)_2[3, 4]C_6H_3.CH_2.CH:CH_2$, boiling at 244°, is present in paracoto oil (A. **271,** 304), in the ethereal oil from *Asarum europæum* (B. 21, 1060), and in *bay oil.* It has been synthetically prepared from pyro-catechol-dimethyl ether, allyl iodide, and zinc dust (B. **28,** R. 1055). Chromic acid oxidises it to dimethyl-proto-catechuic acid or vetraric acid. It forms iso-eugenol-methyl ether when heated with alcoholic potash. It also results when sodium eugenol or potassium chavibetol is treated with methyl iodide (*J. pr. Ch.* 2, **39,** 353).

Safrol, shikimol, *allyl*-3, 4-*pyro-catechol-methylene ether* $CH_2\left\langle\begin{matrix}O[3]\\O[4]\end{matrix}\right\rangle C_6H_3.CH_2.CH:CH_2$, melting at 8° and boiling at 232°, is present in the oil of *Sassafras officinalis* and in that of *Illicium religiosum* or *Shikimino-ki.* Potassium permanganate oxidises it to methylene-p, m-dioxy-benzyl-glycol, homo-piperonylic acid and piperonoyl-carboxylic acid, which are further oxidised to piperonal and piperonylic acid (B. **24,** 3488; **28,** 2088). **Nitrosites** (see B. **28,** R. 1004).

Propenyl-3, 4-pyro-catechin, isomeric with allyl-3, 4-pyro-catechin, is formed in small quantities by transformation of proto-catechin aldehyde with excess of ethyl-magnesium bromide (C. 1908, I. 1624). The propenyl-pyro-catechol ethers: *iso-eugenol, iso-eugenol-methyl ether* and *iso-safrol,* isomeric with the previously described allyl-pyro-catechol ethers, are derived from it.

Iso-eugenol $\left.\begin{matrix}HO[4]\\CH_3O[3]\end{matrix}\right\}C_6H_3CH:CH.CH_3$, boiling at 260°, is formed when homo-ferulic acid is distilled with lime, and upon heating eugenol with caustic potash or sodium alcoholate in amyl alcohol (B. **27,** 2580; C. 1897, I. 384). Synthetically, from vanillin and ethyl-magnesium bromide (C. 1908, I. 1625). On oxidation it yields vanillin, a reaction which is used industrially on a large scale.

Iso-eugenol-methyl ether, *propenyl*-3, 4-*veratrol,* boiling at 263°, has been found in the oil of *Asarum arifolium,* and results upon heating eugenol-methyl ether with alcoholic potash (B. **28,** 1165). Also from methyl-vanillin and C_2H_5MgBr (C. 1908, I. 1625). Potassium perman-

ganate oxidises it to veratroyl-carboxylic acid and veratric acid (B. **24**, 2877). It yields a glycol, melting at 88°, when it is carefully oxidised.

Iso-safrol $CH_2\begin{matrix}O[3]\\O[4]\end{matrix}\}C_6H_3.CH:CH.CH_3$, boiling at 249°, is obtained from safrol by heating it with alcoholic potash, or with dry sodium ethylate. Synthetically, from piperonal and C_2H_5MgI (C. 1904, II. 1566). Potassium permanganate oxidises it to a glycol (B. **36**, 3580), melting at 101°, and piperonoyl-carboxylic acid. Chromic acid changes it to piperonal, artificial heliotropine, from which it can be again re-formed by condensation with propionic acid, and the splitting off of CO_2 from the methylene-homo-caffeïc acid which is first produced (B. **29**, R. 382). Sodium and alcohol reduce it to dihydro-safrol and m-propyl-phenol (B. **28**, 1160). Pseudo-nitrosite, m.p. 128° (A. **332**, 331).

C. **Olefin - trioxy - benzols.—Asarone,** *propenyl-2, 4, 5-trimethoxy-benzene* $(CH_3O)_3[2, 4, 5]C_6H_2.CH:CH.CH_3$, melting at 67° and boiling at 296°, separates from the ethereal oil of the root of *Asarum europæum*, in which it is present together with terpenes and eugenol. Also from calmus oil (B. **35**, 3190), and synthetically from asaryl-aldehyde, propionic anhydride, and sodium propionate (B. **32**, 289).

Potassium permanganate oxidises it to trimethoxy-benzaldehyde and a trimethoxy-benzoic acid, which breaks down into CO_2 and oxy-hydroquinone-methyl ether when it is distilled with lime (B. **28**, 2294).

Elemicin, *allyl-3, 4, 5-trimethoxy-benzol* $(CH_3O)_3[3, 4, 5]C_6H_2CH_2.CH:CH_2$, b.p.$_{10}$ 144°–147°, is the chief constituent of Manila elemi oil (B. **41**, 1768). On oxidation with ozone, it yields trimethyl-homo-gallic aldehyde and trimethyl-homo-gallic acid; with $KMnO_4$, in acetone solution, it forms trimethyl-gallic acid. On heating with alcoholic potash it is converted into the corresponding propenyl compound, *iso-elemicin*, b.p.$_{10}$ 153°–156°, which is geometrically isomeric with asarone. Iso-elemicin is oxidised by ozone to trimethyl-gallic aldehyde or acid (B. **41**, 1918, 2183).

Myristicin, *butenyl-3, 4, 5-trioxy-benzol-methyl-methylene ether* $\begin{matrix}(CH_2O_2)\\(CH_3O)\end{matrix}\}C_6H_2C_4H_7$, melting at 30°, results upon treating the high-boiling portions of *nutmeg oil* and *maci oil* with metallic sodium. It is also obtained with apiol from the seed of French parsley (B. **36**, 3451). Alcoholic potash transposes it into the propenyl compound *iso-myristicin*, m.p. 45°, which, on oxidation with permanganate, gives a methylene-methyl-pyrogallic aldehyde and methylene-methyl-gallic acid (B. **36**, 3446). Nitrosites, see C. 1905, II. 482.

D. **Olefin - tetraoxy - benzols.—Apiol,** *allyl-apionol-dimethyl-methylene ester* $(CH_3O)_2(CH_2O_2).C_6H.CH_2.CH:CH_2$, melting at 30° and boiling at 294°, occurs in parsley seeds and in *Petroselinum sativum*. Potassium permanganate oxidises it to ethers of a tetraoxy-benzaldehyde and a tetraoxy-benzoic acid. See also *Apinol*. Boiling alcoholic potash changes it to the isomeride **isapiol,** m.p. 56°, b.p. 304° (B. **25**, R. 908). An apiol, b.p. 162° (11 mm.), differing from the preceding only in the relative position of the methylene and methyl groups, occurs in the oil from *Anethum græveolens* (B. **29**, 1800), in sea-fennel oil (C. 1909, II. 1334), and in matico oil together with parsley apiol. By alcoholic potash it is converted into the isomeric **dilliso-apiol,** m.p. 44°,

(C. 1904, II. 525) **1-Allyl-2, 3, 4, 5-tetramethoxy-benzol** $(CH_3O)_4$ [2, 3, 4, 5]$C_6HCH_2CH : CH_2$, m.p. 25°, has been isolated from French parsley seed. On oxidation with $KMnO_4$ it yields tetramethoxy-benzoic acid (B. **41,** 2761).

II*b*. **Acetylene-anisol** $CH : CC_6H_4OCH_3$, b.p.$_{11}$ 85°–88°, from *α*, *β*-**dichloro-p-methoxy-styrol** with sodium (B. **36,** 915).

Acetylene-phenetol $CH : C.C_6H_4O.C_2H_5$ (A. **269,** 13).

III*a*. PHENYL-OLEFIN ALCOHOLS WITH THEIR OXIDATION PRODUCTS.

The chemistry of the phenyl-olefin alcohols, aldehydes, and ketones has not been fully developed. Their phenol-like derivatives will be discussed in immediate connection with the most important representatives of the class. The division in detail of the material into poly-alcohols and their oxidation products, as was carried out with uni-nuclear benzene derivatives having oxygen-containing side chains, is not feasible with uni-nuclear benzene derivatives having unsaturated oxygen-containing side chains, because, at present, no representatives have been prepared of many classes of compounds which can be deduced theoretically. The bodies belonging here will, therefore, be introduced at the proper places in connection with the simple phenyl-olefin alcohols, and their oxidation products.

1*a*. **Phenyl-olefin Alcohols.**—The two phenyl-vinyl alcohols, possible theoretically, are not known, and apparently are incapable of existence. The *α*-haloid styrols become aceto-phenone upon replacing their halogen atom by hydroxyl, while the *β*-haloid styrols yield phenyl-acetaldehyde :

α-Chloro-styrol $C_6H_5.CCl : CH_2 \xrightarrow{H_2O} C_6H_5.CO.CH_3$ Aceto-phenone.
ω-Bromo-styrol $C_6H_5.CH : CHBr \longrightarrow C_6H_5.CH_2CHO$ Phenyl-acetaldehyde.

However, the corresponding ethyl ethers have been prepared :

***β*-Phenyl-vinyl-methyl ether,** b.p. 210°–213°, and ***β*-phenyl-vinyl-ethyl ether** $C_6H_5.CH : CH.O.C_2H_5$, b.p.$_{24}$ 115°, are formed from *ω*-chloro-styrol and from phenyl-acetylene by heating with sodium alcoholate (A. **308,** 270 ; C. 1904, I. 720).

***α*-Phenyl-vinyl-methyl ether** $C_6H_5C(O.CH_3) : CH_2$, b.p. 197°, from *β*-methoxy-cinnamic acid.

***α*-Phenyl-vinyl-ethyl ether** $C_6H_5C(OC_2H_5) : CH_2$, b.p. 209°, is obtained by splitting off alcohol from aceto-phenone-acetal, with heat, and is rearranged, by heating under pressure, into isomeric phenyl ethyl ketone (B. **29,** 2931). By saponification these ethers are converted into phenyl-acetaldehyde and aceto-phenone (C. 1904, I. 719).

***β*-Phenyl-vinyl-phenyl ether** $C_6H_5CH : CH.O.C_6H_5$, b.p.$_7$ 158°, by distillation of *α*-phenoxy-cinnamic acid. On heating with alcoholic potash to about 200°, the phenol residue is displaced, and, among other products, *β*-phenyl-vinyl-ethyl ether is formed (B. **38,** 1962).

Cinnamyl alcohol, styrone, *γ*-phenyl-allyl alcohol $C_6H_5.CH : CH CH_2OH$, m.p. 33° and b.p. 250°, occurs as cinnamic ester in liquid *storax*, the sap of the *Liquidambar orientalis* tree, found in the south-western portion of Asia Minor. It is prepared artificially by reduction of cinnamic aldehyde diacetate (C. 1905, II. 672). When oxidised it becomes cinnamic aldehyde, cinnamic acid, and benzoic acid ; see also Stycerine. **Styryl-amine** $C_6H_5.CH : CH.CH_2NH_2$, b.p. 236° (B. **26,**

1858; C. 1906, II. 1420). **Styryl-iso-cyanate** $C_6H_5CH:CH.NCO$, b.p.$_{12}$ 107°, see C. 1909, I. 1655. **α-Phenyl-allyl alcohol** $C_6H_5CH(OH).CH:CH_2$, b.p.$_{25}$ 114°, from phenyl-magnesium bromide and acroleïn (B. **39**, 2554).

Styryl-methyl-carbinol, γ-phenyl-α-methyl-allyl alcohol $C_6H_5.CH:CHCH(CH_3)OH$, b.p.$_{21}$ 144°, from cinnamic aldehyde, with magnesium-methyl iodide (B. **35**, 2649, 3186).

1*b*. **Oxy-phenyl-olefin Alcohols.—β-Anisyl-β-methyl-vinyl alcohol** $CH_3OC_6H_4C(CH_3):CHOH$, m.p. 79°, b.p.$_{14}$ 175°, is formed from estragol dibromide by successive treatment with potassium acetate and alcoholic potash, with simultaneous molecular transposition (C. 1907, II. 1910):

$$\left.\begin{matrix}CH_3OC_6H_4CH_2CHBr.CH_2Br \\ CH_3OC_6H_4CH_2CH(OCOCH_3).CH_2Br\end{matrix}\right\downarrow \nearrow \left.\begin{matrix}CH_3OC_6H_4C(CH_3):CHOH \\ CH_3OC_6H_4CH(CH_3).CHO.\end{matrix}\right\downarrow$$

On distillation at ordinary pressures, and under the influence of acids, the alcohol transposes into p-methoxy-hydratropic aldehyde. With sodium methylate, and dimethyl sulphate, the corresponding methyl ethyl is formed, b.p. 262°, which is also obtained from anethol-methyl-iodo-hydrin by treatment with HgO, with migration of the aromatic residue (C. 1907, II. 1789):

$$CH_3OC_6H_4CH(OCH_3).CHI.CH_3 \longrightarrow CH_3OC_6H_4(CH_3):CHOCH_3.$$

Cumarone $C_6H_4\begin{cases}[1]CH:CH \\ [2]O\text{—}\end{cases}$ is the inner anhydride of o-oxy-phenyl-vinyl alcohol. It will be described later under the heterocyclic compounds.

Glyco-o-cumaro-alcohol $C_6H_{11}O_5.O.C_6H_4.CH:CH.CH_2OH$, m.p. 115°, has been formed from glyco-o-cumaraldehyde (see below).

Sec. methyl-o-cumaro-alcohol $HO.C_6H_4.CH:CH.CH(OH)CH_3$, m.p. 47°. See *Methyl-o-cumaro-ketone*.

Tertiary dimethyl- and **diethyl-o-cumaro-alcohol anhydride** $C_6H_4\begin{cases}CH:CH \\ O\text{—}C(Alk)_2\end{cases}$, b.p.$_{11}$ 93° and b.p.$_{15}$ 127°, from cumarin with magnesium-methyl, and ethyl, iodides (B. **37**, 494).

Coniferyl alcohol, *m-methoxy-p-oxy-styrone* $\begin{matrix}HO[4] \\ CH_3O[3]\end{matrix}\Big\}C_6H_3.CH:CH.CH_2OH$, melting at 73°, is formed from coniferin (*q.v.*), which emulsin decomposes into glucoses and coniferyl alcohol. Vanillin results from its oxidation, and eugenol from its reduction.

Cubebin $CH_2\begin{matrix}O[4] \\ O[3]\end{matrix}\Big\}C_6H_3.CH:CH.CH_2OH$, melting at 125°, is found in cubebs, the fruits of *Piper cubeba*.

1*c*. **Phenyl-acetylene alcohols** are formed by the condensation of sodium-phenyl-acetylene, in ethereal suspension, with trioxy-methylene, and the homologous aldehydes, or by the action of caustic alkali upon a mixture of ketones, with phenyl-acetylene. Also from phenyl-propargyl-aldehyde, and phenyl-acetylene ketones, with alkyl-magnesium haloids: **phenyl-acetylene alcohol** $C_6H_5C:CCH_2OH$, b.p.$_{16}$ 139°; **phenyl-acetylene-methyl-carbinol** $C_6H_5C:C.CH(OH)CH_3$, b.p.$_{29}$ 149°; **phenyl-acetylene-dimethyl-carbinol** $C_6H_5C:C(OH)(CH_3)_2$, m.p. 53°; **œnanthylidene-phenyl-carbinol** $CH_3[CH_2]_4C:CCH(OH)C_6H_5$, b.p.$_{16}$

181°, from sodium-œnanthylidene with benzaldehyde (B. **39,** 2594; C. 1901, II. 25; 1902, I. 619, 1319; 1905, II. 1018; 1907, I. 561).

2a. **Phenyl-olefin Aldehydes.—Cinnamic aldehyde,** *β-phenyl-acrolein* $C_6H_5.CH : CH.CHO$, boiling at 247°, forms the chief constituent of cinnamon oil from *Cinnamomum ceylanicum*, and the oil from *Persea Cassia*, from which it can be extracted with acid sodium sulphite. The first product is the double derivative $C_6H_5.CH : CH.CH(OH)SO_3K$, which combines with a second molecule of mono-potassium sulphite to yield $C_6H_5.CHSO_3K.CH_2.CH(OH).SO_3K+2H_2O$, which dissolves with difficulty (B. **24,** 1805; **31,** 3301).

The aldehyde results from the oxidation of cinnamyl alcohol, in the dry distillation of a mixture of the lime salts of cinnamic and formic acids, and by the action of hydrochloric acid gas or sodium hydrate (B. **17,** 2117), or sodium ethylate (B. **20,** 657) upon a mixture of benzaldehyde and acetaldehyde.

Cinnamic aldehyde is a colourless, aromatic oil, which distils readily in aqueous vapour. When exposed to the air it oxidises to cinnamic acid. It adds chlorine and bromine very readily. The dihaloid addition products change with ease into **α-monochloro-** and **α-monobromo-cinnamic aldehydes** $C_6H_5.CH : CX.CHO$, melting at 35° and 72° (B. **24,** 246).

Cinnamic aldehyde chloride $C_6H_5CH : CH.CHCl_2$, m.p. 54°, b.p.$_{30}$ 143°, behaves like an acid chloride, but combines with chlorine to the **phenyl-tetrachloro-propane** $C_6H_5CHCl.CHCl.CHCl_2$, which is stable in water (C. 1903, I. 457, 1344).

α and ***β*-Trithlo-cinnamic aldehyde** melt at 167° and 213° (B. **24,** 1452).

Hydro-cinnamide $(C_9H_8)_3N_2$ melts at 106°, or at 131° when anhydrous (C. 1898, I. 181).

Cinnamic aldehyde-phenyl-hydrazone $C_6H_5.CH : CH.CH(N_2H.C_6H_5)$ melts at 168°. The *syn-oxime* melts at 138·5°.

Iso-quinolin is produced when the latter is heated with P_2O_5 (B. **27,** 2795). By the action of nitrous gases upon cinnamic aldehyde the chief product obtained is *phenyl-nitro-isoxazol* $\overline{O.N : C(C_6H_5.)C(NO_2) : CH}$ (A. **328,** 196).

Nitro-cinnamic aldehydes are obtained from the aldehydes of the nitro-phenyl-lactic acids. o-, m-, and p-Nitro-cinnamic aldehydes melt at 127°, 116°, and 141° (B. **18,** 2335).

α-Methyl-cinnamic aldehyde $C_6H_5.CH : C(CH_3)CHO$ (B. **19,** 526, 1248).

γ-Benzyl-crotonic aldehyde (*pheno-pentenal*) $C_6H_5CH_2CH_2CH : CHCHO$, b.p.$_{13}$ 139°, from hydro-cinnamic aldehyde with acetaldehyde (B. **31,** 1993).

2b. **Oxy-phenyl-olefin Aldehydes.—o-Cumaric aldehyde,** *o-oxy cinnamic aldehyde* $HO[2]C_6H_4.CH : CH.CHO$, melting at 133°, is produced by the action of emulsin upon *glyco-o-cumaric aldehyde* $C_6H_{11}O_5.O.C_6H_4.CH : CH.CHO$, melting at 199°, the condensation product of helicin (*q.v.*) and acetaldehyde (B. **20,** 1931). It occurs as methyl ether in the oil of cassia (B. **28,** R. 386).

p-Methoxy-cinnamic aldehyde, b.p.$_{14}$ 170°, has been found in tarragon oil (C. 1908, I. 1057).

m- and **p-Oxy-cinnamic-aldehyde-o-acetic acid** $COOH.CH_2O.C_6H_4.CH : CH.CHO$ (B. **19,** 3049).

Piperonyl-acrolein $(CH_2O_2)[3, 4]C_6H_3CH : CH.CHO$, melting at 70°, is obtained from piperonal, acetaldehyde, and sodium hydroxide (B. **27,** 2958); see Piperic acid.

3. **Phenyl-diolefin Aldehydes.—o-Nitro-cinnamylidene-acetaldehyde** $NO_2C_6H_4.CH : CH.CH : CH.CHO$ melts at 153° (B. **17,** 2026).

4*a*. **Phenyl-olefin Ketones.**—The phenyl-olefin ketones are readily obtained by the condensation of aromatic aldehydes with aliphatic ketones, which, besides carbonyl, contain CH_3 or CH_2R groups; from mixed ketones, phenyl-olefin ketones, with normal C-chains, are usually obtained on using NaHO as means of condensation, whereas HCl gives a branched chain (cp. B. **35,** 3088, 3549). Excess of benzaldehyde yields dibenzylidene ketones :

$$C_6H_5CH : CHCOCH_3 \longleftarrow CH_3COCH_3 \longrightarrow C_6H_5CH : CHCOCH : CHC_6H_5.$$

Benzal-acetone, *benzylidene-acetone, styryl-methyl-ketone* $C_6H_5.CH : CH.CO.CH_3$, melting at 41° and boiling at 262°, is produced in the distillation of calcium cinnamate and acetate, as well as in the condensation of benzaldehyde and acetone with dilute sodium hydroxide (A. **223,** 139). Also in small quantities by the action of CH_3MgI upon cinnamic acid nitrite (C. 1906, II. 48).

It dissolves with an orange-red colour in sulphuric aid. With mercaptans, it combines to form mercaptols, which add a third molecule of mercaptan to the olefin linkage $C_6H_5CH(SR)CH_2C(SR)_2CH_3$ (B. **35,** 804).

With alcoholic S_2Am it gives a dimeric benzal-thio-acetone $(C_{10}H_{10}S)_2$, m.p. 132°, which, with water, acids, and salts, gives well-crystallised addition compounds (B. **40,** 2982).

Benzal-acetone-phenyl-hydrazone, m.p. 156°, easily transposes into 1, 6-diphenyl-3-methyl-pyrazolin (B. **20,** 1099). **Oxime,** m.p. 115° (B. **20,** 923). On boiling with sodium hypochlorite, benzal-acetone is broken up into chloroform and cinnamic acid. On reduction, we get benzyl-acetone and, by the junction of two molecules of the olefin ketone, diphenyl-octadiones. Similar behaviour is shown by the homologues of benzal-acetone, on its reduction (B. **35,** 968, 3089). Benzal-acetoxime is reduced by Na and alcohol to **1-phenyl-3-amino-butane** $C_6H_5CH_2CH_2CH(NH_2)CH_3$, by zinc dust and glacial acetic acid, only, to 1-phenyl-3-amino-butene $C_6H_5CH : CHCH(NH_2)CH_3$ (B. **36,** 2997); the latter is split up by ozone into benzaldehyde and α-amido-propionic aldehyde (B. **37,** 615).

o- and **p-Nitro-benzal-acetone,** formed by nitrifying benzal-acetone, melt at 60° and 110° respectively. The o-body passes readily into indigo. α-Methyl-quinaldin results from it by reduction. Water is simultaneously liberated.

p-Amido-benzal-acetone, m.p. 81°, **p-dimethyl-amido-benzal-acetone,** m.p. 132°, by condensation of amido- and dimethyl-amido-benzaldehyde respectively with acetone. Its red and yellow chloride solutions colour wool, silk, and tanned cotton an orange yellow (C. 1906, II. 1324).

α- and γ-**Benzylidene-methyl-ethyl-ketone** $C_6H_5CH : CHCOC_2H_5$, m.p. 39°, b.p.$_{12}$ 142°, and $C_6H_5CH : C(CH_3)COCH_3$, m.p. 38°, b.p.$_{12}$ 127°–130°, and α- and γ-**benzylidene-methyl-propyl-ketone** $C_6H_5CH :$

$CHCOC_2H_7$, b.p.$_{20}$ 155°, and $C_6H_5CH : C(C_2H_5)COCH_3$, b.p.$_{18}$ 120°–130°, with benzaldehyde and methyl-ethyl- and methyl-propyl-ketone respectively, by means of NaHO and HCl respectively. From benzaldehyde and phenoxy-acetone both NaHO and HCl give :

α-Benzylidene-phenoxy-acetone $C_6H_5CH : C(OC_6H_5)COCH_3$, m.p. 102°, which is reduced by alkaline hypochlorite to **α-phenoxy-cinnamic acid** (B. **35,** 3549).

Cuminal-acetone (A. **223,** 147). **Benzal-pinacolin** $C_6H_5CH : CH.COC(CH_3)_3$, m.p. 41°, b.p.$_{25}$ 154°, from benzaldehyde and pinacolin ; it adds malonic acid ester with formation of δ, γ-ketonic acid (B. **30,** 2268).

Phenyl-vinyl-ketone $C_6H_5COCH : CH_2$, b.p.$_{18}$ 115°, a colourless oil of penetrating odour, formed by the action of alcoholic KI solution upon α, β-dibromo-propio-phenone, and by distillation of triphenacyl-methyl-amino-chlorohydrate with steam (B. **39,** 2187). It easily polymerises in sunlight or on heating. $AlCl_3$ converts it into the isomeric α-hydrindone. With HCl, alcohol, and sodium bisulphite it easily combines, with dissolution of the double linkage ; with phenyl-hydrazin it forms 1, 3-diphenyl-pyrazolin (C. 1910, I. 434).

Phenyl-propenyl-ketone $C_6H_5COCH : CH.CH_3$, b.p.$_{20}$ 135°, is also formed from crotonyl chloride, benzene, and $AlCl_3$.

Allyl-aceto-phenone $C_6H_5.CO.CH_2.CH_2.CH : CH_2$, from allyl-benzoyl-acetic acid (B. **16,** 2132), boils at 236°.

4*b*. **Oxy-phenyl-olefin Ketones.**—**o-Oxy-benzal-acetone,** *methyl-o-cumaro-ketone* $HO.C_6H_4.CH : CH.CO.CH_3$, m.p. 139°, is obtained from salicyl-aldehyde, and also by the action of emulsin upon **gluco-methyl-o-cumaro-ketone** $C_6H_{11}O_5.O.C_6H_4.CH_4 : CH.COCH_3$, melting at 192°. The latter compound is a condensation product of helicin (*q.v.*) and acetone (B. **24,** 3180). **p-Oxy-benzal-acetone,** m.p. 103°, from p-oxy-benz-aldehyde, acetone, and HCl, besides the p_2-dioxy-dibenzal-acetone occurring as a chief product (B. **36,** 134) ; **o-, m-** and **p-oxy-benzal-acetone-o-acetic acid,** m.p. 108°, 122°, and 177° (B. **19,** 3056). **Piper-onylidene acetone** $CH_2O_2C_6H_3CH : CHCOCH_3$, m.p. 96° (B. **28,** R. 1009).

5. **Phenyl-acetylene Aldehydes.**—**Phenyl-propargyl aldehyde** $C_6H_5C : C.CHO$, b.p.$_{28}$ 128°, from sodium-phenyl-acetylide with formic acid in ether (C. 1903, II. 569), or, better, from its acetal, easily obtained from α-bromo-cinnamic-aldehyde-acetal, by treating it with dilute mineral acids, is split up by aqueous alkalies, in the cold, into phenyl-acetylene and formic acid. Its oxime $C_6H_5CC.CH : NOH$, m.p. 108°, is isomerised by aqueous alkali to phenyl-isoxazol, and by sodium ethylate further to ω-cyanaceto-phenone $C_6H_5CH_2.CO.CN$ (B. **36,** 3670).

6. **Phenyl-acetylene Ketones** are obtained synthetically from sodium-phenyl-acetylide, with acid esters, chlorides, and anhydrides (C. 1900, I. 1290; II. 1231 ; 1902, I. 404). **Acetyl-phenyl-acetylene** $C_6H_5C : CCOCH_3$, b.p.$_{22}$ 130°, gives, with H_2SO_4, benzoyl-acetone, and is split up by KHO into phenyl-acetylene and acetic acid. **Butyryl-phenyl-acetylene** $C_3H_7COC : CC_6H_5$, b.p.$_9$ 136°. **Benzoyl-amyl-acetylene** $C_6H_5COC : CC_5H_{11}$, b.p.$_{19}$ 178°, from sodium-œnanthylidene with benzoyl chloride, gives, with dilute sulphuric acid, benzoyl-caproyl-methane.

7. **Phenyl-diolefin Ketones.**—**Cinnamyl-acetone** $C_6H_5.CH : CH.CH : CH.CO.CH_3$, m.p. 68°, results from the condensation of cinnamic

aldehyde and acetone. Its **oxime** yields a pyridine derivative upon dry distillation (B. **29,** 613). **Piperonylene-acetone** $(CH_2O_2)C_6H_3.CH : CH.CH : CH.CO.CH_3$, m.p. 89° (B. **28,** 1193). **Benzal-mesityl oxide** $C_6H_5.CH : CH.CO.CH : C(CH_3)_2$, b.p. 178° (14 mm.) (B. **14,** 351). **Piperonylene-acetone** $(CH_2O_2)C_6H_3.CH : CH.CH : CH.CO.CH_3$ melts at 89° (B. **28,** 1193).

8. **Phenyl-olefin-carboxylic Acids.**—These acids arrange themselves in two distinct classes. The one class is derived from a saturated acid, by substituting an unsaturated side chain for hydrogen attached to the benzene nucleus—*e.g. vinyl-benzoic acid.* The second class comprises the phenylated *olefin-monocarboxylic acids.*

A. **Phenyl-olefin-carboxylic acids** (*having their* CO_2H *group attached to the nucleus*).

o-Vinyl-benzoic acid $CH_2 : CH[2[C_6H_4.CO_2H$. o-Vinyl-benzoic acids, chlorinated in the vinyl residue, and also in the benzene residue, have been obtained by the decomposition of chlorinated hydrindene and naphtho-quinone derivatives (B. **27,** 2761 ; A. **275,** 347).

m-Vinyl-benzoic acid, m.p. 95°, is formed from m-amido-styrol (B. **26,** R. 677). **o-, m-,** and **p-Propenyl-benzoic acids** $CH_2 : C(CH_3).C_6H_4.CO_2H$, m.p. 60°, 99°, and 161° (A. **219,** 270 ; **248,** 64 ; **275,** 160).

o-Vinyl-phenyl-acetic acid $CH_2 : CH.C_6H_4.CH_2.CO_2H$. Derivatives of this acid, chlorinated in the vinyl residue, have also been obtained by the breaking down of chlorinated keto-hydro-naphthalenes (B. **21,** 3555).

B. **Phenyl-olefin-carboxylic acids** (*with the carboxyl group in the unsaturated aliphatic side chain*).

The true phenyl-olefin-monocarboxylic acids may be obtained by the oxidation of corresponding alcohols and aldehydes, as well as, by similar methods, from the phenyl-paraffin-monocarboxylic acids or fatty acids. The nuclear-synthetic method, however, is far more important. It consists in the action of the sodium salt, and the anhydride of a fatty acid, upon an aromatic aldehyde (Perkin's reaction).

History.—As early as the year 1856 Bertagnini found that cinnamic acid was formed upon heating benzaldehyde with acetyl chloride. In 1865 W. H. Perkin, sen., synthesised cumarin, the lactone of o-oxy-cinnamic acid, by heating sodium salicyl-aldehyde with acetic anhydride. In 1875 Perkin gave this reaction an entirely different aspect by allowing sodium acetate and acetic anhydride to act upon salicyl-aldehyde. In this modified form the reaction acquired more general application.

Many chemists have assisted in the amplification of the Perkin reaction, which in consequence has become one of the most fruitful synthetic methods.

The course of the reaction has been made clear by the researches of v. Baeyer and O. R. Jackson, Conrad and Bischoff, Oglialoro, and especially by those of Fittig and his students, Jayne and Slocum (A. **215,** 97, 116 ; **227,** 48) :

(1) In the condensation of aromatic aldehydes and fatty acids the carbon atom, combined with the carboxyl group, unites with the carbon of the aldehyde group.

(2) It is doubtful whether the reaction takes place between the aldehyde and the Na salt, or the anhydride of the fatty acid, since,

on using a mixture of anhydride and Na salt of two different acids, we obtain various mixtures of the two possible phenyl-olefin-carboxylic acids, according to circumstances; cp. B. **34**, 918.

(3) The condensation proceeds in two stages: (*a*) the union of the aldehyde and the sodium salt, as in the formation of aldol, with the production of the β-oxy-acid; (*b*) the exit of water from the β-oxy-acid, resulting in the formation of the olefin-carboxylic acid. In many instances the reaction was arrested in the first stage:

(*a*) $C_6H_5.CHO + CH_3.CO_2H \longrightarrow C_6H_5.CH(OH).CH_2.CO_2H.$

(*b*) $C_6H_5.CH(OH)CH_2.CO_2H \xrightarrow{-H_2O} C_6H_5.CH : CH.CO_2H.$

A second nucleus-synthetic method for the preparation of phenyl-olefin-carboxylic acids consists in the condensation of benzaldehydes with fatty-acid esters by means of sodium ethylate or metallic sodium (Claisen, B. **23**, 976):

$$C_6H_5.CHO + CH_3.CO.O.C_2H_5 \xrightarrow{-H_2O} C_6H_5.CH : CH.CO_2.C_2H_5.$$

Phenyl-acrylic Acids.—According to the structural theory there are two possible isomerides, the α- and β-acids, which are also known in cinnamic and atropic acids:

β-Phenyl-acrylic acid, cinnamic acid, $C_6H_5.CH : CH.CO_2H$ α-Phenyl-acrylic acid, atropic acid, $C_6H_5.C(CO_2H)=CH_2$.

Cinnamic acid, *β-phenyl-acrylic acid, acidum cinnamylicum* $C_6H_5.CH : CH.CO_2H$, melting at 133° and boiling at 300°, occurs in Peru and tolu balsams, in storax, and in some benzoïn resins; also, together with α- and β-truxillic acids, the natural iso-cinnamic and allo-cinnamic acids, in the decomposition products of the associated alkaloids of cocaïn.

Formation.—It is produced (1) by the oxidation of its alcohol and its aldehyde; (2) by the reduction of phenyl-propiolic acid with zinc dust and glacial acetic acid (B. **22**, 1181); (3) *nuclear synthesis*—from benzaldehyde: (*a*) with sodium acetate and acetic anhydride, (*b*) with acetic ester and sodium ethylate (see above); (4) upon heating benzyl chloride with sodium acetate. The latter reaction serves for the commercial preparation of cinnamic acid (B. **15**, 969); (5) by heating benzal-malonic acid; (6) its phenyl ester is produced when phenyl-fumaric ester is heated; (7) by splitting off water from synthetic β-phenyl-hydracrylic acid.

Properties and Behaviour.—Cinnamic acid crystallises from hot water in fine needles, from alcohol in thick prisms. It is soluble in 3500 parts of water at 17°, and readily in hot water. It may be purified by distillation under greatly reduced pressure, or by crystallisation from petroleum benzin (A. **188**, 194).

Ferric chloride produces a yellow precipitate in solutions of the cinnamates.

Nitric acid and chromic acid oxidise it to benzaldehyde and benzoic acid. It is converted into phenyl-glyceric acid by potassium permanganate. Fusion with caustic potash decomposes it into benzoic and acetic acids.

Being an unsaturated acid, cinnamic acid can readily take up hydrogen, hydrogen bromide, hydrogen iodide, bromine, chlorine, and

hypochlorous acid, with the production of hydro-cinnamic acid, β-bromo-, β-iodo-hydro-cinnamic acid, phenyl-α, β-dichloro-, α, β-dibromo-propionic acid, or cinnamic acid dichloride, cinnamic acid dibromide, and β-phenyl-α-chloro-lactic acid.

Cinnamic Acid Derivatives.—**Methyl ester** melts at 33° and boils at 263°. It is contained in some *Alpinia* varieties. **Ethyl ester** boils at 271°. **Phenyl ester** melts at 72° and boils at 206° (15 mm.); see Cinnamic acid. **Pyro-catechol ester** melts at 129° (B. **11,** 1220; **18,** 1945; **25,** 3533). **Benzyl ester,** m.p. 30°, also found in the oil of Peruvian balsam (B. **2,** 180).

Styryl ester, *styracin,* melts at 14°. The **chloride** melts at 35° and boils at 154° (25 mm.). The **anhydride** melts at 130° (B. **27,** 284). The **amide** melts at 141°. The **anilide** melts at 151°. The **nitrile** melts at 11° and boils at 254° (B. **15,** 2544; **27,** R. 262).

Unstable and Polymeric Modifications of Cinnamic Acid.—As in the β-alkyl-acrylic acids (Vol. I.), so also in the β-phenyl-acrylic acids, besides the ordinary stable forms, the corresponding unstable stereoisomeric forms have been discovered, and have been termed "allo-cinnamic" acids. Allo-cinnamic acid itself has the noteworthy property of being able to occur in three crystalline forms which are chemically identical but structurally different. These can be converted into one another by the simple process of melting or crystallisation (Bülmann, B. **42,** 182, 1443).

The modification, m.p. 42°, formerly called *Erlenmeyer's iso-cinnamic acid,* is the most unstable, much more so than the modification melting at 58° (formerly *Liebermann's iso-cinnamic acid*), and the modification melting at 168° (formerly *Liebermann's allo-cinnamic acid*).

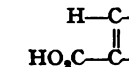
But it is the acid which, with certain precautions, can always be obtained from the mixture of the three liquid acids, or of the three acids, in solution, on precipitation with acid (B. **42,** 4659; **48,** 411). In all reactions which give rise to allo-cinnamic acid it is the primary product, but it is extremely easily transformed into the other acids, especially the stable acid melting at 68°, on contact with the slightest traces of crystals of the other acids. Allo-cinnamic acid is obtained in one or other of its three forms (1) by semi-reduction of phenyl-propiolic acid with hydrogen and colloidal palladium (B. **42,** 3930); (2) by reduction of allo-α- and allo-β-bromo-cinnamic acid with zinc dust in an alcoholic solution; (3) by the action of ultra-violet light upon an alcoholic solution of ordinary cinnamic acid (B. **42,** 4869); (4) by heating benzal-malonic acid, whereby also much ordinary cinnamic acid is formed.

The acid melting at 58° was first discovered in the acids resulting from the breaking up of the secondary cocaïn alkaloids, together with ordinary cinnamic acid.

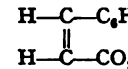
Allo-cinnamic acid, m.p. 68°, forms an aniline salt, m.p. 83°, sparsely soluble in ligroïn. With chlorine and bromine it yields addition products differing from cinnamic dichloride and allo-cinnamic acid dibromide.

On distillation at ordinary pressure by concentrated sulphuric acid and by illumination in benzene solution with the addition of a little iodine, allo-cinnamic acid is converted into ordinary cinnamic acid (B. **28,** 1446). On oxidation with potassium permanganate it forms

phenyl-glycerine acid melting at 21°. On treating with fuming sulphuric acid it splits off water and easily polymerises into *truxone*, in contrast with ordinary cinnamic acid (B. **31**, 2095). On account of this behaviour, but especially of their generation from phenyl-propiolic acid and β-bromallo-cinnamic acid respectively, allo-cinnamic acid is regarded as the maleïnoid or *cis*-form, and ordinary cinnamic acid as the fumaroid or *trans*-form, of β-phenyl-acrylic acid :



Ordinary cinnamic acid



Allo-cinnamic acid.

This view agrees with the behaviour of the oxy-cinnamic acids, in which the spatial configuration can be deduced from the more or less marked tendency towards splitting off H_2O. It is also confirmed by the power of allo-cinnamic acid, in contrast with cinnamic acid, to form with mercuric salts an additive compound of the formula $C_6H_5CH(OH)CH\overset{\frown}{Hg}.COO$, a power which, according to observations with other cis-trans-isomeric olefin-dicarboxylic acids, can only be ascribed to the maleïnoid forms (B. **48**, 568).

By the action of light, in the solid condition cinnamic acid is polymerised into the so-called **α-truxillic acid** $(C_6H_5C_2H_2COOH)_2$ (B. **35**, 2908, 4128), also found in the secondary alkaloids of cocaïn together with β, γ, and δ-truxillic acid. On distillation these acids are split up into ordinary cinnamic acids. They are, perhaps, diphenyl-tetramethylene-dicarboxylic acids. As the heat of combustion is unchanged, the transformation of cinnamic into truxillic acid involves no change of energy, which is noteworthy (*Z. physik. Ch.* **48**, 345).

Haloid Cinnamic Acids substituted in the Side Chain.—(*a*) **Phenyl-monohaloid-acrylic Acids.**—The structural theory provides for two isomeric monochloro-acrylic acids, but there are really two modifications for each of these structural isomerides. It is customary to distinguish them as α- and β-chloro-cinnamic acid and allo-α- and allo-β-chloro-cinnamic acid (B. **22**, R. 741 ; A. **287**, 1).

α-Chloro-cinnamic acid $C_6H_5.CH : CCl.CO_2H$, m.p. 137°, is formed (1) by the action of alcoholic potash or phenyl-α-, β-dichloro-propionic acid ; (2) from benzaldehyde, sodium monochloro-acetate, and acetic anhydride ; (3) from phenyl-α-chloro-lactic acid, by means of acetic anhydride, and sodium acetate ; (4) by the action of CrO_3 upon aldehyde (B. **24**, 249).

Allo-α-chloro-cinnamic acid, m.p. 111°, is produced, together with α-chloro-cinnamic acid, according to method 1.

β-Chloro-cinnamic acid $C_6H_5.CCl : CH.CO_2H$, m.p. 132·5°, and **allo-β-chloro-cinnamic acid,** m.p. 142°, are formed by the addition of hydrochloric acid to phenyl-propionic acid.

α-Bromo-cinnamic acid, $C_6H_5.CH : CBr.CO_2H$, m.p. 130°, and **allo-α-bromo-cinnamic acid,** m.p. 120° (Glaser's β-bromo-cinnamic acid), result when phenyl-α, β-dibromo-propionic acid is acted upon with alcoholic potash. The latter, when heated, changes to the *higher*-melting α-bromo-cinnamic acid. When it is treated with zinc dust in alcoholic solution it yields allo-cinnamic acid. Both yield benzaldehyde upon oxidation.

β-Bromo-cinnamic acid $C_6H_5.CBr : CH.CO_2H$, m.p. 133°, and **allo-β-bromo-cinnamic acid,** m.p. 158·5°, are formed simultaneously upon the addition of hydrogen bromide to phenyl-propiolic acid. The second acid, upon heating, changes to the *lower*-melting β-bromo-cinnamic acid, and upon reduction yields not only cinnamic acid, but also allo-cinnamic acid.

β-Iodo-cinnamic acid $C_6H_5CI : CHCOOH$ is obtained by iodination of cinnamic acid in pyridin solution (C. 1899, II. 527).

(*b*) **Phenyl-dihaloid-acrylic acids** result from the addition of halogens to phenyl-propiolic acid. **Dichloro-cinnamic acid** $C_6H_5.CCl : CCl.CO_2H$, m.p. 120° (B. **25,** 2665). α- and **β-Dibromo-cinnamic acids** melt at 139° and 100° (B. **25,** 2665). **Di-iodo-cinnamic acid** melts at 121° (B. **24,** 4113).

α-Amido-cinnamic acid $C_6H_5.CH : C(NH_2).CO_2H$ decomposes, when rapidly heated, at 240°–250°, with the production of phenyl-vinyl-amine. Its hydrochloride is produced upon heating its benzoyl-amido-cinnamic anhydride with hydrochloric acid to 120°. The acid itself may be liberated from the hydrochloride by means of sodium acetate or soda. The amide of an isomeric (?) α-amido-cinnamic acid, m.p. 160°, is formed by the action of ammonia upon phenyl-dibromo-propionic ester or α-bromo-cinnamic ester (B. **29,** R. 795).

α-Acetamido-cinnamic acid $C_6H_5.CH : C(NHCO.CH_3).CO_2H + 2H_2O$ melts, when anhydrous, at 190° with decomposition. It is formed when sodium hydroxide acts upon the anhydride.

α-Acetamido-cinnamic anhydride $C_6H_5CH : C.N : CCH_3$ (CO—O), melting at 146°, results from the action of acetic anhydride upon α-amido-phenyl-lactic acid, and from glycocoll, benzaldehyde, sodium acetate, and acetic anhydride.

α-Benzoyl-amido-cinnamic anhydride melts at 165°. It is produced in the condensation of hippuric acid and benzaldehyde with acetic anhydride and sodium acetate. When heated with dilute alkalies the lactimide changes to *α-benzoyl-amido-cinnamic acid* $C_6H_5CH : C(NHCOC_6H_5)COOH$, which decomposes at 275° with the formation of phenyl-acetaldehyde and is split up by excess of alkali into benzamide and phenyl-racemic acid (B. **88,** 2036). **p-Oxy-benzoyl-amido-cinnamic acid** anhydride, m.p. 173°, from p-oxy-benzaldehyde, hippuric acid; the corresponding acid is reduced by sodium amalgam to benzoyl-tyrosin.

Cinnamic acids substituted in the benzene nucleus are isomeric with the corresponding mono-cinnamic acid derivatives, having side-chain substitutions.

1. **Monohaloid Cinnamic Acids** have been made from the three nitro-cinnamic acids as bases (B. **16,** 2040; **18,** 961; **25,** 2109).

o-, m-, and **p-Chloro-cinnamic acids** melt at 200°, 176°, and 241°.

o- and **m-Bromo-cinnamic acids** melt at 212° and 178°.

o-, m-, and **p-Iodo-cinnamic acids** melt at 213°, 181°, and 255°.

2. **Nitro-cinnamic Acids.**—The introduction of cinnamic acid into nitric acid of specific gravity 1·5 leads to the formation of the ortho- (60 per cent.) and para-nitro-acids. To separate them, cover the acid mixture with 8–10 parts of absolute alcohol, and conduct hydrochloric

acid gas rapidly into the liquid, until complete solution ensues. On cooling, the para-ester separates. The pure esters are saponified with sodium carbonate or with dilute sulphuric acid, when the pure acids result (A. **212**, 122, 150 ; **221**, 265).

The three isomeric acids can be prepared from the corresponding nitro-benzaldehydes by means of Perkin's reaction :

o-, m-, and **p-Nitro-cinnamic acids,** m.p. 240°, 197°, 286°.
o-, m-, and **p-Nitro-cinnamic ethyl esters,** m.p. 44°, 78°, 138°.

Oxidation converts the three nitro-cinnamic acids into the three nitro-benzaldehydes and nitro-benzoic acids.

Further nitration of o-, m-, and p-nitro-cinnamic acids produces dinitro-cinnamic acids, containing an NO_2 group in the side chain ; **o, p-dinitro-cinnamic acid** $(NO_2)[2, 4]C_6H_3CH : CHCOOH$, m.p. 179°, is obtained from o, p-dinitro-benzaldehyde by means of Perkin's reaction (M. **23**, 534). **m-** and **p-nitro-cinnamic acids** are decomposed at 230° and 220° respectively (C. 1904, II. 1498).

Cinnamic Acids substituted, both in the Benzene Residue and the Side Chain.—*α*, **m-Dinitro-cinnamic acid** $NO_2[3]C_6H_4.CH : C(NO_2)COOH$, from m-nitro-cinnamic acid ester, with nitro-sulphuric acid (A. **229**, 224). *α*, **p-dinitro-cinnamic acid, p-nitro-phenyl-α-nitro-acrylic acid,** from p-nitro-cinnamic acid (A. **229**, 224). See also *ω*, p-Dinitro-phenyl-ethylene and p-Amido-phenyl-alanin. *α*- and ***β*-Nitro-o-amido-cinnamic acid,** m.p. 240° and 254°, from o-amido-cinnamic acid.

3. **Amido-cinnamic Acids** can be prepared by reducing the three mononitro-cinnamic acids with tin and hydrochloric acid. The reduction is better effected with ferrous sulphate in an alkaline solution (B. **15**, 2294 ; A. **221**, 266).

o-, m-, and **p-Amido-cinnamic acids** melt at 158°, 181°, and 176°. When the diazo-bodies are boiled with haloid acids, the haloid cinnamic acids, described above, are produced ; but when they are acted upon with boiling water, the products are *o-*, *m-*, and *p-cumaric acids.*

Carbostyril Formation.—Free o-amido-cinnamic acid differs from o-amido-hydro-cinnamic acid in behaviour, in that, when heated alone, it does not give rise to an inner anhydride formation ; it behaves like o-cumaric acid. The anhydride formation occurs, however, when o-amido-cinnamic acid is heated with hydrochloric acid (B. **13**, 2070), or with 50 per cent. sulphuric acid (B. **18**, 2395). The resulting anhydride is carbostyril, discovered in 1852 by Chiozza, when he reduced o-nitro-cinnamic acid with ammonium sulphide. It can be viewed both as a lactime and a lactame :

Lactame formula, $C_6H_4\begin{cases}[1]CH : CH \\ [2]NH . CO\end{cases}$ Lactime formula, $C_6H_4\begin{cases}[1]CH : CH \\ [2]N : C(OH).\end{cases}$

According to the second formula, carbostyril is nothing more than α-oxy-quinolin ; hence it will be discussed later, in conjunction with quinolin. This will also be done with the alkyl compounds derived from both formulæ.

o-Ethyl-amido-cinnamic acid, m.p. 125° (B. **15**, 1423). Its **nitrosamine** melts at 150° with decomposition, and, on reduction, is condensed to ethyl-isindazol-acetic acid.

4. **o-Hydrazin-cinnamic acid** $NH_2.NH.C_6H_4.CH : CH.CO_2H$, m.p.

171° with decomposition into indazol $C_6H_4\langle^{CH.NH}_{N---}\rangle$ (*q.v.*), and acetic acid.

o - Sulpho - hydrazin - cinnamic acid $SO_3H.NH.NH.C_6H_4CH:CH.CO_2H$ is formed when sodium sulphite acts upon the hydrochloride of o-diazo-cinnamic acid. Hot hydrochloric acid breaks it down into **o-hydrazin-cinnamic acid** and the lactame of this acid $C_6H_4\{^{[1]CH:CH.CO}_{[2]N(NH_2)---}$, m.p. 127° (A. **221**, 274).

5. **Sulpho-cinnamic Acids** are produced when fuming sulphuric acid acts upon cinnamic acid (A. **173**, 8). The m-derivative has been obtained by a nuclear synthesis from m-benzaldehyde-sulphonic acid. p-Sulpho-cinnamic acid, on reduction, splits off the sulpho-groups, and produces hydro-cinnamic acid (B. **33**, 2014; C. 1903, II. 438).

Homologous Cinnamic Acids.—Cinnamic acids containing alkyl groups in the benzene residue are produced when alkylated benzaldehydes are condensed with sodium acetate and acetic anhydride. The three tolyl-aldehydes yield *o-*, *m-*, and *p-methyl-cinnamic acids*, *β, o-*, *m-*, and *p-tolyl-acrylic acids*, melting at 169°, 115°, and 196°. Cuminol yields *p-cumenyl-acrylic acid* $(CH_3)_2CH[4]C_6H_4.CH:CH.CO_2H$, melting at 158°. When the latter is nitrated it yields not only the p-nitro-acid, but also o-nitro-cumenyl-acrylic acid, which manifests the same reaction transpositions as o-nitro-cinnamic acid (B. **19**, 255).

α-Alkyl substituted cinnamic acids are produced in the condensation of benzaldehyde with sodium propionate, capronate, or butyrate and acetic anhydride (A. **227**, 57; B. **34**, 918).

α-Methyl - cinnamic acid, *α-benzal-propionic acid*, *β-phenyl-methacrylic acid* $C_6H_5.CH:C(CH_3)CO_2H$, melting at 78° and boiling at 288°, is also formed from benzyl-propionic ester and metallic sodium (B. **20**, 617). Also from α-methyl-β-phenyl-ethylene-lactic acid by splitting off water (C. 1898, I. 674; B. **20**, 617).

Phenyl-angelica acid, *α-ethyl-cinnamic acid*, *α-benzal-n-butyric acid* $C_6H_5.CH:C(C_2H_5)CO_2H$ melts at 104° (B. **23**, 978).

β-Alkyl-substituted cinnamic acids are obtained by detaching H_2O from β-aryl-alkyl-hydracrylic acids, the condensation products of aromatic ketones with bromacetic ester, and zinc, or iodo-acetic ester, and magnesium, respectively (B. **40**, 1589; **41**, 5).

β-Methyl-cinnamic acid, β-phenyl-crotonic acid $C_6H_5C(CH_3):CHCOOH$, m.p. 98°, b.p. 167°; anilide, from dypnone oxime by Beckmann's transformation (B. **37**, 733). **β-Ethyl-, β-n-propyl-,** and **β-isobutyl-cinnamic acids** melt at 95°, 94°, and 86° respectively.

Higher ω-phenyl-n-olefin-carboxylic acids are produced by heating the lactone-carboxylic acids, when carbon dioxide is expelled, and in the reduction of phenyl-diolefin-dicarboxylic acids.

Phenyl-iso-crotonic acid, *β-benzal-propionic acid* $C_6H_5.CH:CH.CH_2.CO_2H$ melts at 86° and boils at 302° with partial decomposition into water and α-naphthol. It is formed also by expelling CO_2 and rearranging phenyl-paraconic acid, as well as from phenyl-trimethylene-tricarboxylic acid $C_6H_5C(COOH)\langle^{CHCOOH}_{CHCOOH}$ (B. **25**, 1155), by heating; also by heating phenyl-acetaldehyde, malonic acid, and pyridin from the benzal-malonic acid first formed by detaching CO_2, and dis-

placing the double linking (A. **345**, 244). With HBr it combines to γ-phenyl-γ-bromo-butyric acid, which, with soda solution, forms phenyl-butyro-lactone, into which phenyl-iso-crotonic acid can also be partly converted, by means of dilute sulphuric acid or HCl; concentrated HCl condenses phenyl-iso-crotonic acid to a polymeric unibasic lactonic acid, melting at 179° (B. **23**, 3520).

α- and β-**Methyl-phenyl-iso-crotonic acids** melt at 110° and 112° (A. **255**, 262). Δ^2-**Dihydro-cinnamenyl-acrylic acid** $C_6H_5.CH_2.CH:CH.CH_2.CO_2H$, melting at 31°, is formed when sodium amalgam acts upon cinnamenyl-acrylic acid, and also by heating Δ^2- and Δ^1-cinnamylidene-malonic acid. α-**Benzyl-crotonic acid** $C_6H_5CH_2C(:CH.CH_3)COOH$, m.p. 99°, by detaching water from α-benzyl-β-oxy-butyric acid.

The behaviour of these phenyl-olefin-carboxylic acids towards alkalies is worthy of note. While the aliphatic β,γ-unsaturated acids are transposed by alkalies into the isomeric α,β-unsaturated acids (Vol. I.), the aromatic olefin-carboxylic acids show, at the same time, a tendency to place the double linking in the neighbourhood of the phenyl group (cp. Δ^2- and Δ^1-styrols). Thus, the Δ^2-dihydro-cinnamenyl-acrylic acid, with caustic soda, gives a mixture of the Δ^1- and Δ^3-acids (B. **88**, 2742). Phenyl-crotonic acid, on mere heating with pyridin, passes, almost completely, into the phenyl-iso-crotonic acid, a reaction which can be partly reversed by boiling with caustic soda (A. **283**, 309). α-**Benzyl-crotonic acid** gives, on fusing with KHO, phenyl-angelica acid (*J. pr. Ch.* 2, **74**, 334; cp. also A. **319**, 144).

$C_6H_5CH:CH.CH_2.CH_2.CO_2H$ (Δ^3-acid, m.p. 90°) ⟵ $C_6H_5CH_2.CH:CH.CH_2CO_2H$ (Δ^2-Dihydro-cinnamenyl-acrylic acid) ⟶ $C_6H_5CH_2.CH_2CH:CHCO_2H$ (Δ^1-acid, m.p. 104°).

$C_6H_5CH:CH.CH_2.COOH$ (Phenyl-iso-crotonic acid, m.p. 86°) ⟷ $C_6H_5CH_2CH:CH.COOH$ (Phenyl-crotonic acid, m.p. 65°).

$C_6H_5CH_2C(:CHCH_3)COOH$ (α-Benzyl-crotonic acid, m.p. 99°) ⟶ $C_6H_5CH:C(CH_2.CH_3)COOH$ (Phenyl-angelica acid, m.p. 105°).

The Δ^3-dihydro-cinnamenyl-acrylic acid has also been obtained by distillation of δ-phenyl-δ-valero-lactone-γ-carboxylic acid.

Atropic acid, α-phenyl-acrylic acid $C_6H_5.C\begin{matrix}CO_2H\\CH_2\end{matrix}$ melts at 106°. This acid, structurally isomeric with ordinary cinnamic acid, results from tropic acid and atro-lactinic acid when they are heated with concentrated hydrochloric acid or with baryta water. It is sparingly soluble in cold water, easily in ether, carbon disulphide, and benzene, and distils with aqueous vapour. Chromic acid oxidises it to benzoic acid; when fused with caustic alkali it yields formic and α-toluic acids; sodium amalgam converts it into hydro-atropic acid, and hydrochloric and hydrobromic acids change it to α- and β-halogen hydro-atropic acids.

Protracted fusion, or heating with water or hydrochloric acid, converts atropic acid into two polymeric *isatropic acids*, *diatropic acids* $(C_9H_8O_2)_2$ (melting at 237° and 206°), which bear the same relation to atropic acid that the truxillic acids sustain to cinnamic acid (B. **28**, 137).

Methyl-atropic acid $C_6H_5.C\begin{matrix}CH.CH_3\\CO_2H\end{matrix}$, m.p. 135°, is obtained from phenyl-acetic acid and paraldehyde by the action of acetic anhydride (B. **19**, R. 251).

Phenyl-allyl-acetic acid $C_6H_5.CH(CH_2.CH:CH_2)COOH$, b.p. 200°, has been obtained from phenyl-allyl-malonic acid, and its *nitrile* from benzyl cyanide, allyl iodide, and caustic soda (B. **29**, 2601).

III*b*. Oxy-phenyl-olefin-carboxylic Acids.

A. **Monoxy-phenyl-olefin-carboxylic Acids.**—*Formation*:—They are obtained (1) from the corresponding amido-phenyl-olefin-carboxylic acids upon boiling the diazo-compounds with water (B. **14**, 479); (2) by a nuclear synthesis, when the phenol-aldehydes are heated with the sodium salts, and anhydrides, of the fatty acids (Perkin's reaction).

The following nuclear syntheses (von Pechmann) lead to the inner anhydrides or δ-lactones of the o-oxy-cinnamic acids, the so-called cumarins: (3) The action of sulphuric acid upon phenol and malic acid, when it is very probable that the first product is the semi-aldehyde of malonic acid, which condenses with the phenol.

(4) When sulphuric acid is allowed to act upon phenol, and aceto-acetic ester, or monoalkyl-aceto-acetic esters.

Phenol itself, with aceto-acetic ester, gives but a small yield of methyl-cumarin. Polyvalent phenols give cleaner reactions in this respect than simple phenols, and the best are those containing two OH-groups:

3. $C_6H_4\begin{cases}H+CO_2H.CH(OH).CH_2\\OH\qquad\qquad H\end{cases}OCO \longrightarrow C_6H_4\begin{cases}[1]CH:CH\\[2]O—CO\end{cases}$ Cumarin.

4. $C_6H_4\begin{cases}H+CH_3.CO.CH_2\\OH\quad C_2H_5O\end{cases}CO \longrightarrow C_6H_4\begin{cases}[1]C(CH_3):CH\\[2]O———CO\end{cases}$ β-Methyl-cumarin.

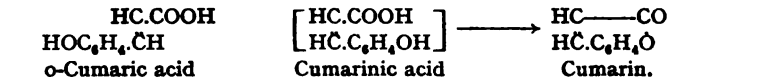
The first members of this series are the monoxy-cinnamic acids obtained by method 1 from the three amido-cinnamic acids. o-Oxy-cinnamic acids are especially important. They, like the cinnamic acids, occur in two stereo-isomeric forms: o-cumaric acids, corresponding to the stable *trans*-form; and cumarinic acids, corresponding to the unstable *cis*-form. The cumarinic acids are in general unstable in the free state, spontaneously detaching water, and passing into the corresponding δ-lactones, the so-called "cumarins." But salts and ethers, both mono- and dialkyl ethers, of the cumarinic acids, are known, which are isomeric with the corresponding compounds of the o-cumaric acids.

The salts and ethers of cumarin are also designated as α-cumarates, and those of o-cumaric acid as the β-cumarates—salts and ethers.

When the hydrogen atom in cumarin, occupying the o-position with reference to phenol-oxygen, is replaced by the nitro-group, *free nitro-cumarinic acid* may be liberated from the salts.

This acid is distinguished from free 3-nitro-cumaric acid in that by the exit of water it reverts to 3-nitro-cumarin. In order to account for the different removability of water in o-cumaric acid and

cumarinic acid respectively, the following space formulæ have been proposed :



As in the case of cinnamic acid, the stable o-cumaric acids and their derivatives may easily be transformed into the unstable cumarinic acids by means of ultra-violet light, *i.e.* by supplying energy in a suitable form. In this action o-cumaric acid yields cumarin direct (B. **44**, 637). By boiling with dilute mineral acids, or by the action of iodine in CS_2 solution, the o-alkyl-cumarinic acids can be transposed into the more infusible o-alkyl-cumaric acids C. (1907, I. 636).

By the action of light in the solid state the o-cumaric acids are transformed into bimolecular bis-cumaric acids, corresponding to the truxillic acids (B. **37**, 1383).

o-Oxy-cinnamic acid, o-cumaric acid HO[2]C_6H_4CH : $CH.CO_2H$, melting at 208°, and isomeric with hydro-cumarilic acid, phenyl-pyro-racemic acid, etc., occurs in *Melilotus officinalis*, together with o-hydro-cumaric acid, and in the leaves of *Angræcum fragrans*. Nitrous acid converts o-amido-cinnamic acid into cumaric acid. It is most readily prepared by boiling cumarin for some time with concentrated potassium hydroxide, or, better, with sodium ethylate (B. **18**, R. 28 ; **22**, 1714). Its acetyl derivative is obtained from salicylic aldehyde and sodium acetate.

Ortho-cumaric acid is very easily soluble in hot water and in alcohol. It does not volatilise with steam. The free cumaric acid heated alone does not yield cumarin, but only when treated with acetic chloride or anhydride. Sodium amalgam converts it into melilotic acid, and fusion with potassium hydroxide into salicylic and acetic acids.

2-Methoxy-cinnamic acid (β) CH_3O[2]C_6H_4[1]CH : $CH.CO_2H$, melting at 182°, is produced by the action of sodium acetate and acetic anhydride upon salicyl-aldehyde-methyl ether, and by the rearrangement of methyl-cumarinic acid. Sodium amalgam reduces it to melilotic acid methyl ether, while bromine changes it to methyl-ether-dibromo-melilotic acid. **o-Cumaric dimethyl ether** (β) CH_3O[2]C_6H_4[1]CH : $CH.CO_2CH_3$, boiling at 293°, is obtained from the previously described acid chloride by means of methyl alcohol. **Aceto-o-cumaric acid** $CH_3.CO.O$[2]$C_6H_4.CH$: $CH.CO_2H$, m.p. 149°, is obtained from salicyl-aldehyde, acetic anhydride, and sodium acetate (B. **20**, 284). See Cumarin.

3-Nitro-cumaric acid (β) NO_2[3]C_6H_3[2](OH)CH : $CH.CO_2H$ is formed by the protracted heating of the dimethyl ether with sodium hydroxide. It suffers no change when heated with water, alcohol, or hydrogen bromide (distinction from 3-nitro-cumarinic acid). The **methyl-ether acid,** m.p. 193°, is formed from 3-nitro-salicyl-aldehyde-methyl ether, and from the *dimethyl ether*, m.p. 88°, by the action of soda (see above). This latter ether is produced when methyl iodide acts upon the silver salt of the methyl-ether acid (B. **22**, 1710).

Cumarin $C_6H_4\begin{cases}\text{[1]CH:CH}\\ \text{[2]O—CO}\end{cases}$, m.p. 70° and b.p. 290°, occurs in

Asperula odorata, in the Tonka beans (from *Dipterix odorata*), and in *Melilotus officinalis*. It is artificially prepared (1) by heating aceto-o-cumaric acid (B. **19**, 287), the reaction product resulting from acetic anhydride and sodium salicyl-aldehyde (A. **147**, 230), or from the action of acetic anhydride and sodium acetate upon salicyl-aldehyde (Perkin, sen., B. **8**, 1599); (2) from phenol with malic acid and sulphuric acid; (3) by reduction of β-chloro- or β-bromo-cumarin.

It has the agreeable odour of *Asperula*, and is applied in perfumery for the preparation of the *Asperula essence*.

Cumarin dissolves rather easily in hot water, and very readily in alcohol or in ether. It dissolves in caustic potash with a yellow colour, the first product being potassium cumarinate, from which carbon dioxide separates cumarin. Boiling concentrated caustic potash changes it to potassium cumarate. In aqueous solution it is reduced by sodium amalgam to melilotic acid, while sodium and alcohol reduce it to oxy-hydro-cinnamic alcohol (B. **39**, 2856).

When it is digested with an aqueous alcoholic solution of potassium cyanide, hydrocyanic acid is added, and, upon subsequent saponification, o-oxy-phenyl-succinic acid is formed (A. **293**, 366). Concerning the action of alkyl-magnesium haloids upon cumarin, see B. **37**, 489.

Cumarin-monomethyl-ester acid, m.p. 88°, and **cumarinic dimethyl ester,** b.p. 275°, result when sodium cumarin is heated to 150° with methyl iodide. When heated, both compounds change to the corresponding o-cumaric acid derivatives, from which they can be recovered by means of ultra-violet light.

Cumaroxime, m.p. 131° (B. **19**, 1662), is produced when hydroxylamine acts upon thio-cumarin.

Cumarin bromide $C_9H_6O_2Br_2$, m.p. 105°, is produced when bromine acts upon cumarin in carbon-disulphide solution. Alcoholic potash converts it into **α-bromo-cumarin** $C_6H_4\begin{cases}[1]CH:CBr\\ [2]O—CO\end{cases}$. Boiling alcoholic potash changes both of these bodies into *cumarilic acid* (*q.v.*). **Thio-cumarin** $C_6H_4\begin{cases}[1]CH:CH\\ [2]O—CS\end{cases}$, m.p. 101°, consists of golden-yellow needles. It is obtained from cumarin or o-cumaric acid by the action of P_2S_5 (B. **19**, 1661).

3-Nitro-cumarinic acid $NO_2[3]C_6H_3\begin{cases}[1]CH:CH.COOH\\ [2]OH\end{cases}$ melts when rapidly heated, with the exit of water, at 150°, and passes, on gentle warming with water or alcohol, into the *anhydride*, *3-nitro-cumarin*, from which it is obtained, upon boiling with soda. It forms long yellow prisms. The silver salt and methyl iodide yield **3-nitro-cumarinic dimethyl ether.**

Cumarin Homologues.—Following method 2 (p. 426), and using propionic, butyric, and iso-valerianic anhydrides, with their sodium salts, the products are *α-alkyl-cumarins*. The *β-alkyl-cumarins* are produced from phenols, aceto-acetic ester, and sulphuric acid (B. **17**, 2188) by method 4. P_2S_5 converts the α-alkyl-cumarins into α-alkyl-thio-cumarins, which hydroxylamine changes to α-alkyl-cumarin oximes (B. **24**, 3459).

α-Methyl-cumarin $C_6H_4\begin{cases}CH:C(CH_3)\\O—CO\end{cases}$, m.p. 90°. **β-Methyl-cumarin** $C_6H_4\begin{cases}C(CH_3):CH\\O—CO\end{cases}$, m.p. 82° (B. **34**, 421).

For other homologous cumarins, see B. **39**, 871; **41**, 830; A. **367**, 232; C. 1906, I. 933; 1908, II. 790; 1909, I. 373.

p-Amido-β-methyl-cumarin, mono- and **dimethyl-amido-β-methyl-cumarin,** m.p. 230°, 123°, and 143°, from amido-, monomethyl-, and dimethyl-amido-phenol with aceto-acetic ester (B. **30**, 277; **32**, 3690).

m-Cumaric acid $HO[3]C_6H_4.CH:CH.CO_2H$, melting at 191°, has been formed from m-amido-cinnamic acid and from m-oxy-benzaldehyde (B. **15**, 2049, 2297).

Nitro-m-cumaric acids, see B. **22**, 292.

o-Amido-m-cumaric acid has been obtained electrolytically from o-nitro-cinnamic acid (B. **27**, 1936).

p-Cumaric acid $HO[4]C_6H.CH:CH.CO_2H$, melting at 206°, is obtained from p-amido-cinnamic acid and from p-oxy-benzaldehyde; also on boiling the extract of aloes with sulphuric acid (preparation, B. **20**, 2528), and by the decomposition of the glucoside naringin (*q.v.*).

Methyl-p-cumaric acid, from anisic aldehyde, melts at 154°. The phenol-alkyl ethers of the cumaric acids yield ethers of unsaturated phenols (see o- and p-vinyl-anisol), just as styrol is obtained from β-bromo-hydro-cinnamic acid by the action of hydrogen bromide, and then a soda solution, when carbon dioxide is eliminated.

β-p-Methoxy-phenyl-methacrylic acid $CH_3O[4]C_6H_4.CH:C(CH_3).COOH$, melting at 154°, is obtained from anisic aldehyde and propionic acid. It breaks down, when heated, into carbon dioxide and anethol.

B. **Dioxy-phenyl-olefin-carboxylic Acids.**—Caffeïc acid, or 3, 4-dioxy-cinnamic acid, corresponding to proto-catechuic acid and umbellic acid, or 2, 4-dioxy-cinnamic acid, are the most important of the known dioxy-cinnamic acids, because they themselves, or their simple derivatives, occur in plants or appear as decomposition products of vegetable substances, and 3-methyl-caffeïc acid, or ferulic acid, can be changed to the valuable vanillin.

Caffeïc acid, *β-3, 4-dioxy-phenyl-acrylic acid, 3, 4-dioxy-cinnamic acid,* and its methyl- and methylene-ester acids, when reduced, become hydro-caffeïc acid and its ether acids. Oxidation yields proto-catechuic acid and its ethers. When the aceto-derivatives of the two methyl-caffeïc acids are oxidised with potassium permanganate, the first products are the aceto-derivatives of the two methyl-ether-proto-catechuic aldehydes. The caffeïc acids and their ether acids can be synthesised from proto-catechuic aldehyde and its ethers with the aid of the Perkin reaction. When fused with caustic potash, caffeïc acid and its ether acids yield proto-catechuic acid and acetic acid:

$C_6H_3\begin{cases}[1]CO:CH.CO_2H\\[3]OH\\[4]OH\end{cases}$	$C_6H_3\begin{cases}[1]CH:CH.CO_2H\\[3]OCH_3\\[4]OH\end{cases}$	$C_6H_3\begin{cases}[1]CH:CH.CO_2H\\[3]OH\\[4]OCH_3\end{cases}$
Caffeïc acid, m.p. 213°	Ferulic acid, m.p. 169° (yields vanillin)	Iso-ferulic acid, m.p. 228° (yields isovanillin).

Caffeïc acid is produced when coffee tannic acid is boiled with potassium hydroxide. It occurs in *Cicuta virosa* (B. **17**, 1922). Ferric

chloride produces a green coloration in its solutions, which sodium carbonate changes to a dark-red colour.

Ferulic acid, *m-methoxy-p-oxy-cinnamic acid*, occurs in the resin of asafœtida, and has been obtained from vanillin as well as from m-methoxy-p-nitro-cinnamic acid, the product resulting from the action of nitric acid upon m-methoxy-cinnamic acid ether (B. **18,** R. 682). Its *aceto-compound* melts at 196°.

Iso-ferulic acid, *m-oxy-methoxy-cinnamic acid, hesperitinic acid*, was first obtained from the glucoside hesperidin (*q.v.*). Both methyl ethers can also be prepared by a partial methylation of caffeïc acid, when the chief product will be iso-ferulic acid. Its *aceto-derivative* melts at 199°.

Dimethyl-caffeic acid $(CH_3O)_2[3, 4]C_6H_3.CH : CH.CO_2H$, melts at 181° (B. **14,** 959).

Piperonyl-acrylic acid $(CH_2O_2)[3, 4]C_6H_3.CH : CH.CO_2H$ melts at 232° (B. **18,** 757).

Diaceto-caffeic acid $(CH_3CO_2)_2[3, 4]C_6H_3.CH : CH.CO_2H$ melts at 190° (B. **11,** 686).

α-Homo-caffeic acid, 3, 4-dioxy-α-methyl-cinnamic acid, melts at 193°. Its monomethyl-ether acid, **homo-ferulic acid** $(CH_3O)(OH)[3, 4]C_6H_3.CH : C(CH_3).COOH$, melting at 168°, yields iso-eugenol when it is heated with lime (B. **15,** 2063).

α-Hydro-piperic acid $(CH_2O_2)[3, 4]C_6H_3CH_2.CH : CH.CH_2.CO_2H$, melting at 78°, is formed when sodium amalgam acts upon piperic acid. When boiled with caustic soda it changes to **β-hydro-piperic acid** $(CH_2O_2)[3, 4]C_6H_3.CH_2.CH_2.CH : CH.CO_2H$, melting at 131°. Sodium amalgam converts the β-acid into *piper-hydronic acid* $(CH_2O_2)[3, 4]C_6H_3[CH_2]_4CO_2H$, melting at 98°.

Umbellic acid, 2, 4-*dioxy-cinnamic acid* $(HO)_2[2, 4]C_6H_3.CH : CH.CO_2H$, decomposes about 240°. It is produced on boiling *umbelliferone* with KHO; the **2, 4-dimethoxy-cinnamic acid,** m.p. 184°, is formed from dimethyl-resorcyl-aldehyde by Perkin's synthesis (C. 1903, I. 580; 1904, I. 724).

Umbelliferone, 4-*oxy-cumarin* $HO[4]C_6H_3\begin{cases}[1]CH:CH\\ [2]O\text{—}CO\end{cases}$, melting at 240°, is found in the bark of *Daphne mezereum*, and is obtained by distilling different resins, such as galbanum and asafœtida. It is obtained synthetically from β-resorcyl-aldehyde by method 2; and also by the condensation of resorcin with malic acid according to method 3. It has an odour resembling that of cumarin, and behaves similarly with caustic potash. Its alkyl ethers show isomeric phenomena analogous to those developed under o-cumaric acid and cumarin (B. **19,** 1778).

β-Methyl-umbelliferone, 4-*oxy*-β-*methyl-cumarin, resocyanin,* $HO[4]C_6H_3\begin{cases}[1]C(CH_3):CH\\ [2]O\text{———}CO\end{cases}$, melting at 185°, is formed when sulphuric acid acts upon resorcin and aceto-acetic ester or acetyl-cyanacetic ester (B. **26,** R. 314). Also from p-amido-methyl-cumarin (B. **26,** R. 314); on melting with potash it gives resaceto-phenone. *Nitro-* and *amido-*methyl-umbelliferone, see B. **34,** 660.

α, β-Dimethyl-umbelliferone melts at 256° (B. **16,** 2127).

The corresponding bodies have been prepared from orcin according to methods 3 and 4 (B. **17**, 1649, 2188)

2, 5-Dioxy-cinnamic acid, m.p. 207°, from o-cumaric acid by oxidation with $KMnO_4$ in alkaline solution (C. 1907, II. 901).

3-Oxy-cumarin, melting at 280°–285° with decomposition, and **5-oxy-cumarin,** melting at 249°, are produced when pyro-catechol and hydroquinone are treated with malic acid and sulphuric acid (B. **18,** R. 333).

5-Oxy-β-methyl-cumarin, m.p. 243°, from hydroquinone, aceto-acetic ester, and sulphuric acid (B. **40,** 2731).

C. **Trioxy-cinnamic Acids.**—Inner anhydrides, δ-lactones of trioxy-cinnamic acids, are **daphnetin,** 3, 4-*dioxy-cumarin*, melting at 255°, and **æsculetin,** 4, 5-*dioxy-cumarin*, the aromatic decomposition products of the isomeric glucosides daphnin and æsculin. Synthetically they have been obtained from pyrogallic aldehyde, or oxy-hydroquinone-aldehyde, acetic anhydride, and sodium acetate (B. **32,** 287).

Æsculetinic and daphnetic acids are the trioxy-cinnamic acids corresponding to these dioxy-cumarins. They are only known as ether acids and ether esters. Potassium permanganate oxidises the triethyl ethers to triethoxy-benzoic acids, which become triethoxy-benzols through the loss of carbon dioxide (B. **15,** 2082; **17,** 1086; **20,** 1119).

Methyl-æsculetin, 4-*oxy*-5-*methoxy-cumarin*, m.p. 203°, is identical with gelseminic acid from *Gelsenium sempervivens*, and also with chrysatropic acid from *Atropa belladonna* (C. 1898, II. 635; B. **31,** 1189).

β-Methyl-æsculetin, 4, 5-dioxy-β-methyl-cumarin, m.p. 270°, from oxy-hydroquinone triacetate with aceto-acetic ester, and sulphuric acid (B. **34,** 423).

Sinapinic acid, *oxy-dimethoxy-cinnamic acid* $(CH_3O)_2[3, 5](OH)[4]C_6H_2CH : CHCOOH$, m.p. 192°, has been obtained from white mustard seeds, and, synthetically, from syringa aldehyde by Perkin's reaction (B. **36,** 1031). **Methyl-sinapinic acid,** 3, 4, 5-*trimethoxy-cinnamic acid*, m.p. 124°, from trimethyl-gallic aldehyde (B. **41,** 2536). **4, 6-Dioxy-cumarin,** m.p. 273°, from phloro-glucin-aldehyde by Perkin's reaction. On methylation it yields **citroptene,** *limettin*, 4, 6-*dimethoxy-cumarin*, m.p. 147°, from the ethereal oils of certain species of *Citrus* (C. 1904, II. 105).

D. **Tetraoxy-cinnamic Acids.—Fraxetin,** melting at 227°, the aromatic decomposition product of the glucoside of fraxin (*q.v.*), contains the monomethyl ether of a trioxy-cumarin. Isomerides of fraxetin have been prepared synthetically (B. **27,** R. 130; **29,** R. 293).

E. **Phenyl-acetylene-carboxylic Acids.—Phenyl-propiolic acid** $C_6H_5.C : C.CO_2H$, m.p. 136°, is obtained by boiling α- and β-bromo-cinnamic acids with alcoholic potash, by acting upon sodium phenyl-acetylene with carbon dioxide (1870, Glaser, A. **154,** 140), and when the latter, and sodium, act upon ω-bromo-styrol. It is prepared by boiling the dibromide of cinnamic acid, or its ethyl ester, with alcoholic potash (B. **34,** 3647; **36,** 902). Heated in water to 120°, it decomposes into phenyl-acetylene and CO_2. On heating with acetic anhydride, or by the action of $POCl_3$, phenyl-propiolic acid passes into the anhydride of 1-phenyl-naphthalin-2, 3-dicarboxylic acid (B. **40,** 3372; C. 1908, II. 1357). Similarly, phenyl-propiolic ester polymerises, on

heating to 200°, to form phenyl-naphthalin-dicarboxylic ester (B. **40,** 3839; see the formation of trimesinic acid from propiolic acid).

On adding hydrogen, by means of sodium amalgam, it becomes hydro-cinnamic acid; treated with zinc dust and glacial acetic acid, or sodium and alcohol, it becomes cinnamic acid (B. **22,** 1181); with hydrogen in the presence of colloidal palladium, allo-cinnamic acid; and, by addition of HCl and HBr, it yields β-halogen and allo-β-halogen-cinnamic acid. It unites with halogens to form phenyl-dihalogen-acrylic acids; with hydrazin hydrate and phenyl-hydrazin it forms 3-phenyl-pyrazolone and 1, 3-diphenyl-pyrazolone (B. **27,** 783). Similarly, phenyl-propiolic acid unites with other amine bases (C. 1900, I. 547; 1908, I. 233), as well as the sodium compound of β-diketones, aceto-acetic ester, and malonic ester. In the last-mentioned reaction a tricarboxylic acid is obtained which, on discarding CO_2, becomes phenyl-glutaconic acid (B. **27,** R. 163; C. 1899, II. 608). On digesting with sodium alcoholates one or two molecules of alcohol are attached, and β-alkoxy-cinnamic ester is formed, or dialkyl acetals of benzoyl-acetic ester (C. 1904, I. 659; 1906, I. 1551). Phenyl-propiolic-acid nitrile unites with one molecule of a primary or secondary amine to form β-alkyl-amido-cinnamic-acid nitriles, such as $C_6H_5C(NHCH_3) : CH.CN$, which, with acids, regenerate the amine and form benzoyl-aceto-nitrile (C. 1906, II. 1842).

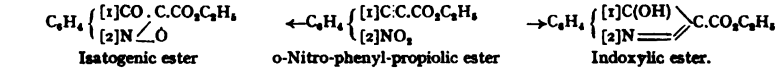
Phenyl-propiolic ethyl ester $C_6H_5C : C.CO_2C_2H_5$, b.p.$_{22}$ 153°, is also formed from sodium-phenyl-acetylide, with chloro-carbonic ester. It easily transforms into benzoyl-acetic ester by hydration (A. **308,** 280). Phenyl-propiolic acid nitrile $C_6H_5C : CCN$, m.p. 39°, is formed from the amide with P_2O_5; from sodium-phenyl-acetylide with gaseous HCN; and from phenyl-propargyl-aldoxime with acetic anhydride (B. **36,** 3671). Chloride, b.p.$_{25}$ 131°; amide, m.p. 102° (B. **25,** 3537; **29,** R. 795; C. 1906, I. 651).

o-Nitro-phenyl-propiolic acid decomposes at 156°. It is obtained when alcoholic potash acts upon the dibromide of o-nitro-cinnamic acid (Baeyer, A. **212,** 140). When boiled with water it decomposes into carbon dioxide and o-nitro-phenyl-acetylene. When boiled with alkalies it yields isatin.

It dissolves in concentrated sulphuric acid, with conversion into the *isomeric isatogenic acid,* which, at once, forms carbon dioxide and isatin. Its *silver salt* explodes with great violence when it is heated.

If digested with alkaline reducing agents (grape-sugar and potassium hydroxide, ferrous sulphate, hydrogen sulphide, potassium xanthate), *it readily changes to indigo blue* (Baeyer, 1880; B. **13,** 2259).

The *ethyl ester* of the acid is obtained by conducting hydrochloric acid gas into a mixture of the acid and alcohol. It melts at 60°–61°. When it is dissolved in sulphuric acid it changes to the isomeric isatogenic ester. Ammonium sulphide reduces it to the indoxylic ester (B. **14,** 1741):



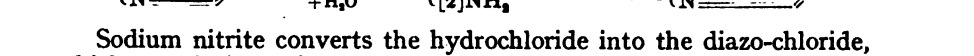
p-Nitro-phenyl-propiolic acid, m.p. 198°, is formed from the p-nitro-cinnamic ester after the same manner as the ortho-acid. When boiled with water it breaks up into carbon dioxide and p-nitro-phenyl-acety-

lene. It yields p-nitro-aceto-phenone if digested at 100° with sulphuric acid.

The **ethyl ester,** m.p. 126°, when digested with sulphuric acid at 35°, forms p-nitro-benzoyl-acetic acid.

o-Amido-phenyl-propiolic acid melts at 129° with decomposition into CO_2 and o-amido-phenyl-acetylene. It is obtained by reducing o-nitro-phenyl-propiolic acid with ferrous sulphate and ammonia (B. **16,** 679). It separates as a yellow crystalline powder. When boiled with water it yields o-amido-aceto-phenone.

γ-Chloro-carbo-styril results when the acid is boiled with hydrochloric acid, and γ-oxy-carbo-styril upon heating it with sulphuric acid (B. **15,** 2147) :



Sodium nitrite converts the hydrochloride into the diazo-chloride, which at 70° yields cinnolin-oxy-carboxylic acid.

m-Methyl-phenyl-propiolic acid $CH_3[3]C_6H_4C : C.CO_2H$ melts at 109° (B. **20,** 1215).

F. **Phenyl-diolefin-carboxylic acids** have been prepared from cinnamic aldehyde by means of the Perkin reaction. **Cinnamylidene-acetic acid,** *cinnamenyl-acrylic acid* $C_6H_5.CH : CH.CH : CH.CO_2H$ melts at 165°, from cinnamic aldehyde, pyridin, and malonic acid with heat, by decomposition of the cinnamylidene-malonic acid first formed together with the stereo-isomeric allo-cinnamylidene-acetic acid, m.p. 138° ; on overheating it discards CO_2 and passes into phenyl-butadiene (B. **35,** 2696).

The *nitrile,* boiling at 285°, is obtained from cinnamenyl-cyano-acrylic acid. The o- and p-nitro-acids, melting at 217° and 271°, were obtained from o- and p-nitro-cinnamenyl-acetone by the action of NaClO (A. **258,** 356). The *o-amido-acid* melts with decomposition at 176° (B. **18,** 2332). **Cinnamenyl-crotonic acid** and **cinnamenyl-angelica acid** melt at 157° and 126° (C. 1906, I. 349).

Piperic acid, 3, 4-*methylene-dioxy-cinnamenyl-acrylic acid* $(CH_2O_2)[3, 4]C_6H_3.CH : CH.CH : CH.CO_2H$, melting at 217°, is produced, together with piperidin, when piperin is boiled with alcoholic potassium hydroxide. It can be synthesised by aid of the Perkin reaction, from piperonyl-acrolein, and from piperonylene-malonic acid (B. **28,** 1190). Sodium amalgam converts it into two **isomeric hydro-piperic acids,** α and β. It combines with four atoms of bromine. It is oxidised, in dilute solution by potassium permanganate at 0°, to piperonal and racemic acid (B. **28,** 2372). When fused with potassium hydroxide it breaks down into acetic, oxalic, and proto-catechuic acids. Its chloride and piperidin form piperin (*q.v.*).

History.—Fittig and Mielck (1874) determined the constitution of piperic acid. Ladenburg and Scholtz (1894) effected its synthesis (B. **27,** 2958).

α-Methyl- and **α-ethyl-piperic acids,** melting at 208° and 179°, were synthesised just like piperic acid (B. **28,** 1187).

β-Cinnamylidene-propionic acid $C_6H_5CH : CH.CH : CH.CH_2COOH$, m.p. 112°, is formed, in small quantities, on condensation of cinnamic aldehyde and sodium succinate with acetic anhydride (A. **331,** 162).

IV. Compounds which may be viewed as Oxidation Products of Mononuclear-aromatic Polyalcohols with Unsaturated Side Chains.

The domain of the aromatic polyalcohols having unsaturated side-chains has been even less completely, and even more irregularly, developed than that of the polyhydric aromatic paraffin alcohols and their oxidation products. At present the alcohols and aldehydes are wholly lacking; from them the carboxylic acids and their derivatives belonging here can be theoretically deduced. Consequently the material in this section will not be sharply differentiated, although, in the main, the classification is the same as that observed with the oxidation products of the aromatic polyparaffin alcohols.

1. *Phenylene-oxy-olefin-carboxylic Acids.—Methylene-phthalide* and *iso-cumarin* are inner anhydrides, or lactones, of the possible o-vinyl-alcohol-benzoic acids. They are not known in a free state. Cumarin is isomeric with them.

Methylene-phthalide $C_6H_4\begin{cases}[1]C=CH_2\\ \diagdown\\ [2]COO\end{cases}$, m.p. 59°, is formed in the distillation of phthalyl-acetic acid. Its **dibromide** melts at 98°. **Monobromo-methylene-phthalide** $C_6H_4\begin{cases}[1]C=CHBr\\ \diagdown\\ [2]CO.O\end{cases}$ is produced by the action of bromine upon o-aceto-phenone-carboxylic acid. **Dichloro-methylene-phthalide** $C_6H_4\begin{cases}[1]C=CCl_2\\ \diagdown\\ [2]COO\end{cases}$ melts at 128°. It is formed, together with **tetrachloro-methyl-phthalide** $C_6H_4\begin{cases}CCl.CCl_3\\ \diagdown\\ COO\end{cases}$, melting at 93°, upon conducting chlorine into a mixture of glacial acetic acid and phthalyl-chloracetic acid (A. **255**, 383; **268**, 294).

Bromo-methylene-phthalide, m.p. 140°, from aceto-phenone-o-carboxylic acid, with bromine. **Dibromo-methylene-phthalide,** m.p. 140°, from α-dibromaceto-phenone-o-carboxylic acid on heating with concentrated sulphuric acid (B. **40**, 83).

Derivatives of *methylene-phthalimidin* $C_6H_4\begin{cases}[1]C=CH_2\\ \diagdown\\ [2]CO.NR\end{cases}$ have been prepared by the action of amines and amino-acids upon o-aceto-phenone-carboxylic acid (B. **29**, 2518).

Nitro-methylene-phthalide $C_6H_4\begin{cases}C=CHNO_2\\ \diagdown\\ CO.O\end{cases}$, m.p. 207° with decomposition, from phthalic anhydride and nitro-methane, is split up by alkali to **nitro-phenacyl-o-carboxylic acid** $NO_2CH_2COC_6H_4COOH$, m.p. 121° (B. **36**, 570).

Ethylidene-phthalide $C_6H_4\begin{cases}[1]C=CH.CH_3\\ \diagdown\\ [2]COO\end{cases}$ melts at 64° (B. **19**, 838).

Propylidene- and iso-butylidene-phthalides, boiling at 170° (12 mm.) and melting at 97°, are obtained by condensing phthalic anhydride with the sodium salts and anhydrides of propionic, butyric, and iso-valeric acids. Water and carbon dioxide are eliminated (B. **29**, 1436).

These alkylidene phthalides are transposed by sodium ethylate into the isomeric diketo-hydrindenes. By alkaline hydrates, they are

split up into o-ketone-carboxylic acids. Ethylene-phthalide gives rise to propio-phenone-o-carboxylic acid.

Iso-cumarin $C_6H_4\begin{cases}[1]CH=CH\\ [2]CO—O\end{cases}$, melting at 47° and boiling at 285°, is formed in the distillation of silver iso-cumarin-carboxylate. It readily volatilises with steam. When digested with soda it becomes :

Anhydro-o-oxy-vinyl-benzoic acid $O(CH : CH[2]C_6H_4.CO_2H)_2$, melting at 183°. When this body is heated with hydrochloric acid to 160° the *anhydride* $O(CH : CH[2]C_6H .CO)_2O$, melting at 234°, results. The *imide* $O(CH : CH[2]C_6H_4CO)_2NH$, melting at 285°, is produced when alcoholic ammonia acts upon the anhydride at 170° (B. **27**, 207).

Iso-carbo-styril $C_6H_4\begin{cases}[1]CH=CH\\ [2]CO—NH\end{cases}$, melting at 208°, is isomeric with carbo-styril, the lactame corresponding to iso-cumarin. It is formed when iso-cumarin is heated to 130° with alcoholic ammonia, and upon heating iso-carbo-styril-carboxylic acid or its silver salt. It yields iso-quinolin when distilled with zinc dust (B. **27**, 208).

3-Methyl-iso-cumarin $C_6H_4\begin{cases}[1]CH=C.CH_3\\ [2]CO—O\end{cases}$, melting at 118°, is formed when *ψ-diacetyl-cyano-benzyl-cyanide* $C_6H_4\begin{cases}[1]C=C(O_2CCH_3)CH_3\\ [2]CN\ CN\end{cases}$, melting at 135°, is heated to 180° with hydrochloric acid. This latter body results from the action of sodium acetate and acetic anhydride upon o-cyano-benzyl cyanide (B. **27**, 831). Similarly, o-cyano-benzyl cyanide furnishes an additional series of homologues of iso-cumarin, all of which are characterised by their ready transposition into iso-carbo-styrils (see B. **29**, 2543, etc.).

Ammonia converts 3-methyl-iso-cumarin into the corresponding 3-*methyl-iso-carbo-styril*, melting at 211° (B. **25**, 3563).

By boiling in KHO methyl-iso-cumarin is transformed into methyl-benzyl-ketone-o-carboxylic acid.

Bergaptene $\left.\begin{matrix}CH=CH\\ \vert\\ —O\end{matrix}\right\}C_6H(OCH_3)\begin{cases}CH=CH\\ \vert\\ O—CO\end{cases}$ (?), melting at 188°, appears to be a derivative of oxy-vinyl-cumarin. It separates, on standing, from raw bergamot oil, which is obtained by pressing out the fresh rinds of *Citrus Bergamia*, Risso (B. **26**, R. 234).

2. *Phenylene-aldehydo-carboxylic Acids.*—**p-Aldehydo-cinnamic acid** $CHO[4]C_6H_4.CH : CH.CO_2H$, melting at 247°, is obtained from terephthal-aldehyde by the Perkin reaction (A. **231**, 375 ; B. **34**, 2784).

3. *Phenylene-dicarboxylic Acids.*—**o-Cinnamyl-carboxylic acid** $CO_2H[2]C_6H_4.CH.CH.CO_2H$, m.p. 174°, reverts again to phthalidacetic acid. It is produced when phthalidacetic acid is digested with alkalies, and by carefully oxidising β-naphthol with potassium permanganate (B. **21**, R. 654). More energetic oxidation produces carbo-phenyl-glyoxylic acid.

o-Cyano-cinnamic acid $CN[2]C_6H_4CH : CH.CO_2H$, m.p. 252°, is produced when sodium acetate and acetic anhydride act upon α-cyano-benzal chloride, and also from o-amido-cinnamic acid (B. **24**, 2574 ; **27**, R. 262). Its formation from the Na salt of β-nitroso-naphthol $C_6H_4\begin{cases}C(NO) : C(OH)\\ \vert\\ CH=CH\end{cases}$ by heating to 250° is worthy of note (C. 1901, I. 69).

p-Cinnamyl-carboxylic acid is obtained from terephthal-aldehydic acid and sodium acetate. It is an insoluble, infusible powder (A. **231**, 369).

o-Phenylene-diacrylic acid $C_6H_4[1,2](CH:CH.CO_2H)_2$ melts above 300°. It is produced when alcoholic potash acts upon o-xylylene-dichloro-dimalonic ester, or from o-phthal-aldehyde by Perkin's reaction (B. **19**, 435; A. **847**, 117).

p-Phenylene-diacrylic acid is obtained from p-aldehydo-cinnamic ester with sodium acetate and acetic anhydride (A. **231**, 377), and from p-xylylene-dibromo-dimalonic ester (B. **34**, 2784).

4. *Phenyl-olefin-ketols.*—**Oxy-methylene-aceto-phenone** $C_6H_5.CO.CH:CH.OH$, when separated from its sodium compound, is a very unstable oil. Its sodium derivative is formed when sodium ethylate acts upon formic ester and aceto-phenone. Formerly, oxy-methylene-aceto-phenone was considered to be *benzoyl-acetaldehyde*. As to the constitution of the oxy-methylene compounds, see Vol. I. With phenyl-iso-cyanate it yields an O-carbanilido-derivative, m.p. 125°, which, by the action of potassium carbonate, is easily transposed to the isomeric C-carbanilide, m.p. 94° (B. **37**, 4631). Phenyl-hydrazin converts it into diphenyl-pyrazol (*q.v.*); hydroxylamine unites with it to form benzoyl-acetaldoxime. See also Benzylidene phenoxy-acetone.

5, 6. *Phenyl-oxy-olefin- and diolefin-carboxylic Acids.*—**Oxy-methylene-phenyl-acetic ester** $C_6H_5C(CO_2C_2H_5):CHOH$—see Formyl-phenyl-acetic ester.

β-Methoxy-cinnamic ester $C_6H_5C(OCH_3):CHCO_2C_2H_5$, b.p.$_{14}$ 155°, and **β-ethoxy-cinnamic ester,** b.p.$_{16}$ 168°, are formed from phenyl-propiolic acid ester with sodium alcoholate, and from benzoyl-acetic ester with ortho-formic acid ether. The corresponding acids melt at 180° and 162° respectively, discarding CO_2 and forming β-phenyl-vinyl-methyl and ethyl ethers (B. **29**, 1005; C. 1904, I. 659, 719). **β-Phenoxy-cinnamic ester** $C_6H_5C(OC_6H_5):CHCOOC_2H_5$, m.p. 76°, b.p.$_{10}$ 265, is obtained by attaching sodium phenolate to phenyl-propiolic acid ester; the acid, m.p. 143°, yields on heating CO_2 and β-phenoxy-styrol $C_6H_5C(OC_6H_5):CH_2$ (C. 1900, II. 247; 1901, II. 410, 1052; 1906, I. 1551). **α-Phenoxy-cinnamic acid** $C_6H_5CH:C(OC_6H_5)COOH$, m.p. 181°, is obtained from benzaldehyde, sodium phenoxy-acetate, and acetic anhydride by synthesis; also from benzylidene-phenoxy-acetone with alkali hypochlorite by disintegration (B. **35**, 3555). On heating it partly decomposes into CO_2 and ω-phenoxy-styrol, partly into CO and phenyl-acetic phenyl ester (B. **38**, 1958).

γ-Phenyl-α-oxy-crotonic acid, styrol-α-oxy-acetic acid $C_6H_5CH:CH.CH(OH)COOH$, m.p. 137°, is prepared by saponifying its nitrile, **cinnamyl-aldehyde cyano-hydrin,** m.p. 74°, with cold concentrated hydrochloric acid; or by reduction of cinnamyl-formic acid with Na amalgam. On boiling with hydrochloric acid the acid is readily rearranged to benzoyl-propionic acid (B. **37**, **3124**), whereas by boiling with NaHO benzyl-pyro-racemic acid is formed. Heated alone or with acetic anhydride, benzoyl-propionic acid yields **γ-phenyl-Δ^{α}-croto-lactone** $C_6H_5\overline{C:CH.CH_2COO}$, m.p. 91°, from which benzoyl-propionic acid is easily regenerated. Another derivative of phenyl-

α-oxy-crotonic acid is probably **trichloro-methyl-styrol-carbinol** $CCl_3CH(OH)CH : CHC_6H_5$, m.p. 67°, obtained from cinnamic aldehyde with chloroform, which, on heating with water, or alkalies, also yields benzoyl-propionic acid (A. **299**, 1 ; C. 1900, II. 238).

β-Benzyl-angelica-lactone $C_6H_5.CH_2C\begin{cases}CH_2—CO\\ C.(CH_3)O\end{cases}$ is obtained in the distillation of benzyl-lævulinic acid.

β-Oxy-cumarin $C_6H_4\begin{cases}[1]C(OH) : CH\\ [2]O———CO\end{cases}$, m.p. 206°, is formed from its carboxylic ester by saponification and detachment of CO_2. In its properties, solubility in alkaline carbonate, formation of an oximido-compound with sodium nitrite, capacity of condensation with aldehydes, etc., it resembles the aliphatic tetronic acids, and it has therefore also been called **benzo-tetronic acid.** On heating with concentrated alkalies, oxy-aceto-phenone is formed (A. **379**, 333). **β-Ethoxy-cumarin,** m.p. 174°, is formed, from the silver salt, with IC_2H_5. With PCl_5 and PBr_5, β-oxy-cumarin gives **β-chloro-** and **β-bromo-cumarin,** m.p. 92° and 91° respectively, which are reduced with zinc dust and alcohol to cumarin.

Methylene-bis-benzo-tetronic acid $\left(C_6H_4\begin{cases}C(OH) : C\\ O———CO\end{cases}\right)_2CH_2$, m.p. about 206°, and **ethylidene-bis-benzo-tetronic acid,** m.p. 165°, from benzo-tetronic acid with formaldehyde and acetaldehyde respectively (A. **367**, 169). Homologous and substituted β-oxy-cumarins have been prepared by starting from the corresponding substituted salicylic chlorides (A. **367**, 219 ; **368**, 23).

δ-Oxy-cinnamylidene-acetic Acid.—Its lactone is **phenyl-cumalin** $C_6H_5.C : CH.CH : CH.CO$ (O———), melting at 68°, and found in *coto bark* (B. **29**, 2659 ; R. 1116).

From a phenyl-oxy-triolefin-carboxylic acid we derive **cinnamylidene-dimethyl-croto-lactone** $C_6H_5CH : CH.CH : \overset{O———CO}{C.C(CH_3) : C(CH_3)}$, m.p. 153°, obtained by condensation of phenyl-iso-crotonic acid and pyro-cinchonic anhydride (A. **306**, 242).

7. *Phenyl-dioxy-olefin-carboxylic Acids.*—**Oxy-methylene-phthalide** $C_6H_4\begin{cases}[1]C=CHOH\\ [2]CO.O\end{cases}$, m.p. 148°, from ω-bromo-aceto-phenone-o-carboxylic acid on boiling with water ; with hydroxylamine and phenyl-hydrazin, it reacts in the desmotropic form as formyl-phthalide, with the formation of an oxime, m.p. 152°, and a phenyl-hydrazone, m.p. 180° with decomposition (B. **40**. 74).

8, 9. *Phenyl-olefin- and diolefin-α-keto-carboxylic Acids* result from the condensation of aromatic aldehydes with pyro-racemic acid.

Cinnamyl-formic acid $C_6H_5.CH : CH.CO.CO_2H$, a light yellow rubber-like mass, from benzaldehyde, pyro-racemic acid, and HCl. With NaHO we obtain the acid in bright flakes $+H_2O$, melting at 57° when anhydrous ; on reduction with a sodium amalgam it gives γ-phenyl-α-oxy-crotonic acid (B. **36**, 2527). The syrupy acid is also formed from its nitrile, **cinnamyl cyanide** $C_6H_5.CH : CH.CO.CN$, m.p. 114° (B. **14**, 2472).

o-Nitro-cinnamyl-formic acid $NO_2[2]C_6H_4.CH : CH.CO.COOH$, m.p.

135°, from o-nitro-benzaldehyde with pyro-racemic acid. It is converted into indigo by alkalies in the cold, discarding oxalic acid.

3, 4-Methylene-dioxy-cinnamyl-formic acid $(CH_2O_2)[3, 4]C_6H_3.CH : CH.CO.CO_2H$, m.p. 149°, and **piperonylene-pyro-racemic acid** $(CH_2O_2)[3, 4]C_6H_3CH : CH.CH.CH.CO.CO_2H$, m.p. 166°, are formed from piperonal and piperonyl-acroleïn.

Cinnamylidene-pyro-racemic acid $C_6H_5CH : CH.CH : CH.COCOOH$, m.p. 107°, from cinnamic aldehyde and pyro-racemic acid, is reduced by sodium amalgam to the corresponding α-oxy-acid, which is transformed, by boiling with HCl, into δ-benzal-lævulinic acid (B. **37**, 1318).

10. *Phenyl-olefin-β-ketone-carboxylic Acids* result from the condensation of aceto-acetic ester, and aromatic aldehydes, with hydrochloric acid gas, or, better, with primary or secondary amines in the cold (B. **29**, 172). **Benzal-aceto-acetic ester** $C_6H_5.CH : C\langle^{CO_2C_2H_5}_{COCH_3}$, m.p. 59°, b.p. 181° (17 mm.) (A. **281**, 63). The m-*nitro*-ester melts at 112° (B. **26**, R. 448). **γ-Benzal-diethyl-aceto-acetic ester** $C_6H_5.CH : CH.COC(C_2H_5)_2.CO_2C_2H_5$, m.p. 101°. **Acetyl-cumarin** $C_6H_4\{^{[1]CH : C.COCH_3}_{[2]O\text{—}CO}$, m.p. 124°, from aceto-acetic ester, salicyl-aldehyde, and acetic anhydride. It has feebly acid qualities; see Cumarin and nitro-cumarin (B. **35**, 1153; **37**, 4497). See also Acetyl-oxy-cumarin.

Allyl-benzoyl-acetic ester $C_6H_5.CO.CH.\langle^{CO_2C_2H_5}_{CH_2.CH : CH_2}$ melts at 122° (B. **16**, 2132).

γ-Phenyl-α-acetyl-crotonic lactone $C_6H_5\overline{C : CH.CH(COCH_3)COO}$, m.p. 113°, from aceto-phenone-aceto-acetic ester on boiling with alcoholic KOH (B. **39**, 1809).

11. *Phenyl-olefin- and diolefin-γ-ketone-carboxylic Acids* result by the condensation (1) of aldehydes and ketone-carboxylic acids with acids or alkalies; (2) of olefin-dicarboxylic anhydrides—*e.g.* maleïc-acid anhydride, citraconic anhydride, and benzols with aluminium chloride.

β-Benzoyl-acrylic acid $C_6H_5.CO.CH : CH.CO_2H$ melts at 96° when anhydrous. It results from the action of sulphuric acid upon maleïc anhydride (see above), as well as from phenyl-γ-keto-α-oxy-butyric acid. Also from bromo-benzoyl-propionic acid with potassium acetate, and from phenyl-iso-crotonic acid with sodium hypo-iodide (C. 1908, I. 1175; 1909, I. 530).

Trichloro-ethylidene-aceto-phenone $C_6H_5.CO.CH : CH.CCl_3$, melting at 102°, is produced when sulphuric acid acts upon chloral-aceto-phenone. **β-Benzoyl-crotonic acid** $C_6H_5.CO.C(CH_3) : CH.CO_2H$, melting at 113°, is obtained from citraconic anhydride (B. **15**, 891).

β-Benzal-lævulinic acid $C_6H_5.CH : C\langle^{CO.CH_3}_{CH_2.CO_2H}$, melting at 125°, is produced by the condensation of benzaldehyde and lævulinic acid in *acid solution*. It parts with water upon distillation and forms 3-aceto-1-naphthol. Phenyl-itaconic acid is formed by its oxidation, and β-benzyl-lævulinic acid by its reduction. Hydroxylamine produces the neutral *lactoxime, benzal-lævoxime* $C_6H_5.CH : C\langle^{CH_2CO}_{CH_3/C : N.O}$, melting at 94°.

When benzaldehyde and lævulinic acid condense in *alkaline solution* the product is :

δ-Benzal-lævulinic acid $C_6H_5CH : CH.CO.C_2H_4.CO_2H$, melting at 120°. It yields *benzal-angelic lactone*, melting at 90° (B. **24,** 3202), upon distillation.

δ-Cinnamal-lævulinic acid $C_6H_5CH : CH.CH : CH.CO.CH_2.CH_2.CO_2H$, m.p. 161°, sulphur-yellow crystals, from cinnamic aldehyde, lævulinic acid, and pyridin (B. **38,** 1113).

12, 13. *Phenyl-olefin- and diolefin-dicarboxylic Acids.*—**Benzal-malonic acid** $C_6H_5.CH : C(CO_2H)_2$, melts with production of cinnamic acid and allo-cinnamic acid. It is formed in the condensation of benzaldehyde, malonic acid, and glacial acetic acid. By heating a mixture of benzylidene-aniline, and similar bodies, with malonic acid, cinnamic acid is obtained at once (B. **31,** 2596). Its *ethyl ester*, boiling at 198° (13 mm.), is obtained from benzaldehyde, malonic ester, and hydrochloric acid. It adds to itself more readily than the free acid. Aniline as well as phenyl-hydrazin converts the methyl ester into **β-anilido-** and **β-phenyl-hydrazido-benzyl-malonic methyl ester**, melting at 117° and 94° (B. **29,** 813). When substituted benzaldehydes are used, substituted benzal-malonic acids result—*e.g.* **nitro-benzal-malonic acid,** which is reduced by ferrous sulphate and ammonia to β-carbo-styril-carboxylic acid (B. **21,** R. 253).

α-Cyano-cinnamic acid, *semi-nitrile of benzal-malonic acid* $C_6H_5.CH : C\langle^{CO_2H}_{CN}$, melting at 180°, is obtained by the action of cyano-acetic acid in the heat upon benzaldehyde, or when it is boiled with cyano-acetyl chloride. When heated it passes into the nitrile of cinnamic acid. The *methyl* and *ethyl esters* melt at 70° and 50°. A large number of semi-nitriles of unsaturated, aromatic malonic acids of related constitution have been obtained by the union of readily accessible, aromatic aldehydes with cyano-acetic acid (B. **27,** R. 262). *Nitrile-acid amide, dinitrile*, and *diamide* of benzal-malonic acid, melting at 123°, 87°, and 190°, have also been synthesised by the condensation of benzaldehyde with cyano-acetamide, malonitrile, and malonamide (B. **28,** 2251 ; **35,** 1320).

Benzal-barbituric acid $C_6H_5.CH : C\langle^{CO.NH}_{CO.NH}\rangle CO$ is easily formed from benzaldehyde and malonyl-urea (B. **34,** 1340).

β-Carbo-styril-α-carboxylic acid $C_6H_4\{^{[1]CH : C.CO_2H}_{[2]NH.CO}$ is formed from o-amido-benzaldehyde upon heating it with malonic acid to 120°, and also from o-nitro-benzal-malonic acid (B. **21,** R. 353). Its silver salt, when heated, yields carbo-styril.

Cumarin-α-carboxylic acid $C_6H_4\{^{[1]CH : C.CO_2H}_{[2]O—CO}$, melting at 187°, breaks down at 290° into carbon dioxide and cumarin. It is obtained from salicyl-aldehyde, malonic acid, and glacial acetic acid or amine bases (B. **31,** 2593, 2597), as well as from—

α-Cyano-cumarin $C_6H_4\{^{[1]CH : C.CN}_{[2]O—CO}$ melting at 182°. This latter body may be prepared by the action of dilute sulphuric acid upon

o-oxy-benzal-dicyano-acetic ester $HO[2]C_6H_4CH[CH(CN)CO_2C_2H_5]_2 + \frac{1}{2}H_2O$, melting at 140°. This is a condensation product of salicyl-aldehyde and cyano-acetic ester (B. **27**, R. 576).

α-Cumarin-carboxylic amide, m.p. 269°. Anilide, m.p. 250° (C. 1906, II. 724). Cp. also **β-Oxy-cumarin-α-carboxylic ester.**

Cinnamylidene-malonic acid, *phenyl-butadiene-dicarboxylic acid* $C_6H_5.CH : CH.CH : C(COOH)_2$, m.p. 208°, has a yellow colour, but, on illumination, it passes into a colourless, dimeric modification which on oxidation yields α-truxillic acid, and therefore probably also contains the tetramethylene ring. Concentrated sulphuric acid restores the yellow, monomolecular form (B. **35**, 2411; C. 1902, II. 1047). On heating, cinnamylidene-malonic acid splits off CO_2 and gives a mixture of linkage-isomeric forms of cinnamylidene-acetic acid. Methyl and ethyl ester, m.p. 67° and 36°. Reduced with Na amalgam, the acid gives 1, 4-hydro-cinnamylidene-malonic acid $C_6H_5CH_2CH : CH.CH(COOH)_2$, m.p. 107° with decomposition, which, on heating with NaHO, passes into the isomeric **3, 4-hydro-cinnamylidene-malonic acid** $C_6H_5CH_2CH_2 CH : C(COOH)_2$, m.p. 116° with decomposition (A. **306**, 259). **Cinnamylidene-cyano-acetic acid** $C_6H_5.CH : CH.CH : C(CN)CO_2H$, m.p. 212°.

Piperonylene-malonic acid $(CH_2O_2)[3, 4]C_6H_3.CH : CH.CH : C(CO_2H)_2$ melts at 205° with decomposition into CO_2 and piperic acid (B. **28**, 1190). **Phenyl-allyl-malonic acid** $C_6H_5C(CH_2.CH : CH_2)(COOH)_2$ melts with decomposition at 145°. Its ester is formed when allyl iodide acts upon phenyl-malonic ester (B. **29**, 2600).

Phenyl-maleic acid $\begin{matrix} CH.CO_2H \\ \| \\ C_6H_5.C.CO_2H \end{matrix}$, changes below 100° into its *anhydride*, melting at 119°, which is produced when bromine and PBr_3 act upon phenyl-succinic acid, and the reaction product is treated with water. Phenyl-malic acid is formed simultaneously (B. **23**, R. 573).

Cumarin-β-carboxylic acid $C_6H_4\begin{cases} C(COOH) : CH \\ O \text{———} CO \end{cases}$, m.p. 180°, is decomposed into CO_2 and cumarin, during the dry distillation of its silver salt; its ethyl ester, m.p. 78°, is formed from phenol, oxalic-acid ester, and sulphuric acid (B. **34**, 422); from resorcin, oxalic-acid ester, and sodium alcoholate we obtain **umbelliferone-β-carboxylic acid**, *resorcyl-maleïnic lactone* $HO[4]C_6H_3\begin{cases} C(COOH) : CH \\ O \text{———} CO \end{cases}$, m.p. 248° (B. **34**, 381).

Phenyl-itaconic acid $\begin{matrix} C_6H_5.CH : C.CO_2H \\ | \\ CH_2.CO_2H \end{matrix}$, m.p. 172°, is formed (1) from succinic ester, benzaldehyde, and sodium ethylate; (2) from phenyl-paraconic ester and sodium ethylate. When fused, particularly under reduced pressure, it separates into water and its *anhydride*, melting at 163°–166°, which, in every fusion, changes in a slight degree to isomeric **phenyl-citraconic anhydride**, melting at 60°. Water changes the latter to **phenyl-citraconic acid**, melting at 103°–106°. If phenyl-citraconic acid in chloroform solution, to which a little bromine is added, be exposed to sunlight, it becomes **phenyl-mesaconic acid**, melting at 212°. On boiling with NaHO these isomeric acids are partly transformed into a fourth isomeric acid, **phenyl-aticonic acid** $\begin{matrix} C_6H_5CH \\ \| \\ HO_2C.C.CH_2COOH \end{matrix}$,

m.p. 149°–151°, which is stereo-isomeric with phenyl-itaconic acid. By the action of concentrated sulphuric acid it easily discards water and passes into **indone-acetic acid** $C_6H_4\begin{cases}CH\\CO\end{cases}\!\!>C.CH_2CO_2H$, the phenyl-itaconic acid only furnishing the corresponding anhydride. From this the *cis*-position of the phenyl and carboxyl in phenyl-aticonic acid has been deduced (cp. Vol. I. and A. **304,** 130 ; **305,** 35 ; **330,** 292 ; B. **41,** 3983).

Cumarin-propionic acid $C_6H_4\begin{cases}[1]CH=C.CH(CH_3)CO_2H\\[2]O\text{——}CO\end{cases}$, m.p. 171°, is formed, together with o-oxy-phenyl-methyl-iso-crotonic acid, from salicyl-aldehyde, sodium pyro-racemate, and acetic anhydride. It passes into α-ethyl-cumarin when it is distilled (A. **255,** 285).

Methyl-phenyl-itaconic acid $C_6H_5C(CH_3)=C(CO_2H)CH_2.CO_2H$ melts with decomposition at 161°–163°. It is obtained from succinic ethyl ester, aceto-phenone, and sodium ethylate in ether. Its anhydride melts at 114°. This acid may, like phenyl-itaconic acid, be transformed into several isomerides (B. **37,** 1619).

Styril-succinic acid, *cinnamenyl succinic acid* $C_6H_5CH : CH.CH(COOH).CH_2COOH$, m.p. 173°, is obtained by saponifying the resultant product of the action of alcoholic potassium cyanide upon cinnamylidene malonic ester (cp. phenyl-succinic acid, and A. **306,** 254).

Cinnamylidene-succinic acid, *styril-itaconic acid, cinnamenyl-itaconic acid* $C_6H_5CH : CH.CH : C(COOH)CH_2COOH$, m.p. 215°–218° with decomposition, from cinnamic aldehyde, succinic ester, and sodium ethylate, is reduced by sodium amalgam to phenyl-ethylidene-pyro-tartaric acid $C_6H_5CH_2CH : CHCH(COOH)CH_2COOH$, m.p. 112°. This latter acid transposes, on boiling with NaHO, to phenyl-ethyl-itaconic acid $C_6H_5CH_2CH_2CH : C(COOH).CH_2COOH$, m.p. 153° (B. **34,** 2188 ; cp. A. **331,** 151).

Phenyl-glutaconic acid $C_6H_5.C(CH_2.COOH) : CH.COOH$, m.p. 154°, has been obtained from the condensation product formed in the union of phenyl-propiolic ester with sodium-malonic ester. Its ester, $b.p._{11}$ 187°, is converted by ammonia into **γ-phenyl-α, α_1-dioxy-pyridin** (C. 1899, I. 1081 ; B. **27,** R. 163 ; A. **370,** 72).

Benzal-glutaric acid $C_6H_5.CH : C(CO_2H)CH_2.CH_2.COOH$ (A. **282,** 338) melts at 177° (B. **31,** 2004).

Benzyl-glutaconic ester $C_6H_5.CH_2.CH(COOH)CH : CH.COOH$ melts at 145° (A. **222,** 261). Its *ethyl ester*, boiling at 203° (10 mm.), when treated with aqueous ammonia at 100°, forms *benzyl-dioxy-pyridin* (B. **26,** R. 318).

Cinnamenyl-glutaric acid $C_6H_5CH : CH.CH(CH_2CO_2H)_2$, m.p. 135°, is obtained from the condensation product of cinnamenyl-acrylic ester and sodium-malonic ester, or by oxidation of cinnamenyl-dihydro-resorcin with sodium hypochlorite (A. **345,** 206).

14. *Phenyl-olefin-tricarboxylic Acids.*—**Phenyl-carboxy-aconitic ester** $C_6H_5C(CO_2C_2H_5)_2C(CO_2C_2H_5) : CHCO_2C_2H_5$ and **benzyl-carboxy-aconitic ester** from phenyl- and benzyl-malonic esters, with chloro-fumaric ester (C. 1902, II. 888).

15. *Phenyl-oxy-olefin-dicarboxylic Acids.*—**Cinnamenyl-paraconic acid** $C_6H_5CH : CH.\underline{CH.CH(CO_2H)CH_2.CO}$, m.p. 145°, from cinnamic

aldehyde and succinic acid. On boiling with water it yields cinnamenyl-crotonic acid (C. 1906, II. 515).

β-Oxy-cumarin-α-carboxylic ethyl ester $C_6H_4\begin{cases}C(OH):CH.CO_2C_2H_5\\O\text{———}CO\end{cases}$, m.p. 101°, is formed by the condensation of acetyl-salicylic-acid chloride with sodium-malonic ester, and detachment of NaCl and acetic ester. In a similar manner we obtain **β-oxy-α-cyano-cumarin,** m.p. 242°, and **β-oxy-α-acetyl-cumarin,** m.p. 134°, from acetyl-salicylic chloride and sodium cyano-acetic ester or aceto-acetic ester (A. **367,** 169).

16. *Phenylene-oxy-olefin-dicarboxylic Acids.*—Phthalyl-acetic acid and iso-cumarin-carboxylic acid have the same relation to each other that methylene-phthalide sustains to iso-cumarin. Phthalyl-acetic acid and its homologues have been obtained by applying the Perkin reaction to phthalic anhydride:

Phthalyl-acetic acid $C_6H_5\begin{cases}C=CH.CO_2H\\\diagdown\\COO\end{cases}$ melts with decomposition above 260°. When distilled under greatly diminished pressure it breaks down into carbon dioxide and methylene-phthalide. Salts of benzoyl-aceto-carboxylic acid are obtained by dissolving it in alkalies. When it is heated with water to 200° it breaks down into carbon dioxide and o-acetyl-benzoic acid. When heated with ammonia it forms *phthalimide-acetic acid.* The alkylamines react analogously.

Sodium ethylate converts phthalyl-acetic acid into the sodium salt of diketo-hydrindene-carboxylic acid (*q.v.*) (B. **26,** 953).

Iso-cumarin-carboxylic acid $C_6H_4\begin{cases}[1]CH=C\text{—}CO_2H\\\quad\quad|\\[2]CO\text{—}C\end{cases}$, melting at 237°, is formed when o-carbo-phenyl-glyceric-acid lactone is heated to 160° with hydrochloric acid; see Iso-cumarin. Ammonia converts it quite readily into **iso-carbo-styril-carboxylic acid** $C_6H_4\begin{cases}[1]CH=C.CO_2H\\\quad\quad|\\[2]CO\text{—}NH\end{cases}$, melting at 320° (B. **25,** 1138). Boiling caustic potash decomposes it into o-toluic acid and oxalic acid (B. **28,** R. 770).

On the formation of γ-oxy-iso-carbo-styril-carboxylic ester from phthalyl-glycocollic ester, see the latter.

Oxy-methylene-homophthalic ethyl ester $C_6H_4\begin{cases}C(:CHOH).CO_2C_2H_5\\CO_2C_2H_5\end{cases}$, a colourless oil of strong acid reaction, obtained by the condensation of homophthalic ester with formic ester. On heating to 100° it passes into **iso-cumarin-4-carboxylic ethyl ester** $C_6H_4\begin{cases}C(CO_2C_2H_5):CH\\CO\text{———}O\end{cases}$, m.p. 68°, which is split up again into formic acid and homophthalic acid by alkalies. Ammonia converts the ester into **iso-carbo-styril-4-carboxylic ethyl ester** $C_6H_4\begin{cases}C(CO_2C_2H_5):CH\\CO\text{———}NH\end{cases}$, m.p. 227° (B. **41,** 3253).

17. *Phenylene-oxy-olefin-tricarboxylic Acids.*—**Phthalyl-malonic ester** $C_6H_4\begin{cases}[1]C=C(CO_2C_2H_5)_2\\\diagdown\\[2]COO\end{cases}$, melting at 74°, is formed, together with phthalyl-dimalonic ester, from phthalyl chloride and sodium-malonic ester (A. **242,** 46). **Phthalyl-cyano-acetic ester** $C_6H_4\begin{cases}[1]C=C\begin{matrix}CO_2C_2H_5\\CN\end{matrix}\\\diagdown\\[2]COO\end{cases}$,

melting at 175°, is made from phthalyl chloride and sodium-cyano-acetic ester (B. **26**, R. 370).

B. Hydro-aromatic Substances with Single-nucleus, Hydro-benzol Derivatives.

It was shown in the introduction to the carbocyclic compounds that the treatment of the hydro-aromatic derivatives presupposed a knowledge of the aromatic bodies. Indeed, numerous reactions which led to the hydro-aromatic compounds, especially the additions, were described in connection with the aromatic substances. Many bodies discussed under the aromatic derivatives—*e.g.* the quinones—are rather to be viewed as derived from the hydro-aromatic hydrocarbons. And synthetic reactions were also studied in the discussion of the fatty bodies which will again be encountered.

The methods of ring formation in cyclo-paraffins, discussed at the commencement of this volume, are also used to some extent in the building up of hydro-aromatic substances. The *terpenes* and *camphor* will be included in the hydro-aromatic derivatives, as they are closely related to the hydrated m- and p-cymols.

(1) Hydro-aromatic Hydrocarbons.

Hexahydro-benzol is the parent hydrocarbon of the hydro-aromatic substances. Tetra- and dihydro-benzol bear the same relation to it that an olefin and a diolefin show to the paraffin, having the same number of carbon atoms.

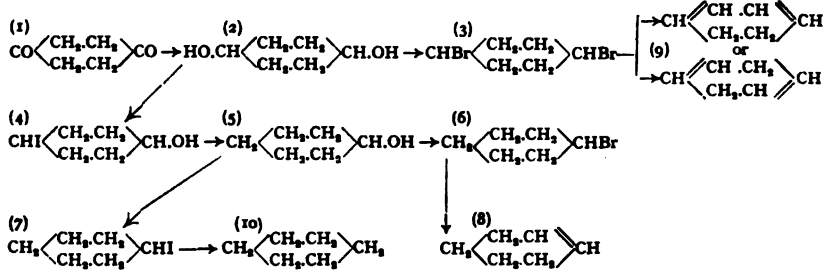
The hexahydro-benzols, which are isomerides of olefins with a like number of carbon atoms, resemble the paraffins in chemical behaviour; they belong to the cyclo-paraffins, while the tetrahydro-benzols belong to the cyclo-olefins, the dihydro-benzols to the cyclo-diolefins, and benzene is the simplest imaginable cyclo-triolefin, if we accept the formula proposed for it by Aug. Kekulé.

The aromatic compounds in general oppose a great resistance to the attachment of hydrogen. This was only overcome in 1897 by an excellent method discovered by Sabatier and Senderens, which consists in conducting the vapours of aromatic substances, with excess of hydrogen, over finely divided hot nickel. By this means it is easy to convert aromatic hydrocarbons, phenols, and anilines into the corresponding hydro-aromatic compounds.

Berthelot (1867) first effected the reduction of benzene to hexahydro-benzol. It was obtained pure by Baeyer (1894) in the course of an investigation in which he demonstrated how the simplest representatives of the hydro-aromatic bodies—hexahydro-benzol, tetrahydro-benzol, and dihydro-benzol—could be prepared from p-diketo-hexamethylene, a decomposition product of succino-succinic ester. Before beginning a detailed description of the hydro-aromatic hydrocarbons, it may be well briefly to present the steps of this research in a diagram. The enclosed numbers following the names refer to the formulæ of the diagram.

p-Diketo-hexamethylene (1) yields quinite (2) by reduction, which hydrogen bromide changes to p-dibromo-hexamethylene, and hydrogen iodide into the mono-iodo-hydrin (4) of quinite, along with p-di-iodo-

hexamethylene. Quinite mono-iodo-hydrin, when reduced, yields oxy-hexamethylene (5), obtained more easily from pimelin-ketone and cyclo-hexanone. Hydrogen bromide and iodide convert oxy-hexamethylene (6) into bromo- and iodo-hexamethylene (6, 7). When p-di-bromo-hexamethylene and monobromo-hexamethylene are heated with quinolin, the latter yields *tetrahydro-benzol* (8) and the former dihydro-benzol (9); whereas mono-iodo-hexamethylene is reduced by zinc dust and glacial acetic acid to *hexahydro-benzol* (10):



The following values (V) and differences (D) were observed by Stohmann in determining the heats of combustion and the boiling-points of benzene, the three hydro-benzols, and hexane:

			Approximately.
C_6H_6 (V) = 779·8	D = 68·2 Cal.	b.p. 80·4°	D = + 5°
C_6H_8 „ = 848·0	„ = 44·0 „	„ 84°–86°	„ = − 2°
C_6H_{10} „ = 892·0	„ = 41·2 „	„ 82°–84°	„ = − 3°
C_6H_{12} „ = 993·2	„ = 58·0 „	„ 79°–79·5°	„ = −10°
C_6H_{14} „ = 991·2		„ 69°	

The differences calculated from these numbers would have to be equal if the changes were of like character. The magnitude of these differences expresses, therefore, the magnitude of the changes involved in the reduction (A. **278**, 115).

(1*a*) Cyclo-hexanes, Hexahydro-benzols (Naphthenes).

Hydro-aromatic hydrocarbons constitute the chief portion of Caucasian petroleum (I. 88) (Beilstein and Kurbatow, B. **18**, 1818). Markownikow has, therefore, designated them naphthenes.

The simplest naphthene, hexahydro-benzol, is also called hexa-naphthene, and its homologues are called heptanaphthene, octo-naphthene, nononaphthene, etc. Besides these hexahydra-benzols, we also find in Caucasian petroleum the isomeric alkyl pentamethylenes (cp. B. **31**, 1803; *Ch. Zeitung*, **22**, 900; A. **324**, 1). Hexahydro-benzols have also been discovered in the tar from bituminous coal and in that from certain shales, as well as in the *resin oils* obtained from the distillation of colophonium.

Finally, a nononaphthene, hexahydro-pseudo-cumol, has been found in coal-tar (C. 1908, II. 402). Artificially, the hexahydro-benzols are prepared from their halogen substitution products by reduction, or by transposition with alkyl-magnesium haloids. They are obtained most easily by reduction of the benzene hydrocarbons, on passing the latter, in the gaseous state, mixed with hydrogen, over finely divided

nickel at temperatures of 180° to 250°. In the benzol homologues, with lengthy side chains, this is accompanied by a partial breaking up of the latter. Thus, from propyl-benzol we obtain, besides propyl-cyclo-hexane, a small quantity of ethyl- and methyl-cyclo-hexane. At temperatures above 300° the cyclo-hexanes are broken up by the nickel, particularly in the hydrogen and the corresponding benzene hydrocarbons (C. 1901, I. 502, 817; II. 201). They have been made artificially by reducing aromatic hydrocarbons with hydriodic acid at high temperatures. Hexahydro-benzol resists decomposition by means of hydrogen very strongly (A. **278,** 88). The hexahydro-benzols are more easily obtained by reducing their halogen substitution products.

When hydro-iodic acid is used as a reducing agent, under certain circumstances alkyl-pentamethylenes appear to form by a process of isomerisation; these are isomeric with the hexamethylenes. Thus methyl-pentamethylene is formed together with hexamethylene (B. **30,** 1214; A. **324,** 6).

The hexahydro-benzols are distinguished from the olefins isomeric with them by their higher specific gravity, and their inability to take up bromine. Like the paraffins, they are first changed by chlorine or bromine into monohalogen substitution products.

Heating with dilute nitric acid produces nitro-substitution products; tertiary H atoms are replaced by the NO_2 group with particular ease (A. **301,** 154; **302,** 1; C. 1899, I. 176; 1910, II. 1376). With nitro-sulphuric acid small quantities of nitrified benzol hydrocarbons are produced. The action of bromine and aluminium bromide converts the hexahydro-benzols into substitution products of aromatic hydrocarbons:

Cyclo-hexane, *hexahydro-benzol*	m.p. 6·4°,	b.p.	81°	D_{20} 0·7788 [1]
Methyl-cyclo-hexane, *hexahydro-toluol*	„	„	100°	„ 0·7697 [2]
1, 1-Dimethyl-cyclo-hexane	„	„	120°	D_{15} 0·7864 [3]
1, 2-Dimethyl-cyclo-hexane, *hexahydro-o-xylol*	„	„	126°	D_{20} 0·7733 [4]
1, 3-Dimethyl-cyclo-hexane, *hexahydro-m-xylol*	„	„	121°	„ 0·7736 [4]
1, 4-Dimethyl-cyclo-hexane, *hexahydro-p-xylol*	„	„	120°	„ 0·7690 [4]
Ethyl-cyclo-hexane	„	„	130°	„ 0·7772 [4]
1, 2-Methyl-ethyl-cyclo-hexane	„	„	151°	„ 0·784 [5]
n-Propyl-cyclo-hexane	„	„	156°	„ 0·7865 [6]
1, 3, 5-Trimethyl-cyclo-hexane, *hexahydro-mesitylene*	„	„	138°	„ 0·7867 [4]
1, 3, 4-Trimethyl-cyclo-hexane, *hexahydro-pseudo-cumol*	„	„	143°	„ 0·7807 [4]
1, 3, 5-Dimethyl-ethyl-cyclo-hexane	„	„	169°	„ 0·7929 [7]
1, 4-Methyl-iso-propyl-cyclo-hexane, *hexahydro-cymol*	„	„	167°	see Terpene.

Literature.—[1] B. **34,** 2799. [2] A. **341,** 129. [3] C. 1905, II. 1673. [4] C. 1901, II. 201. [5] C. 1909, I. 851. [6] B. **34,** 2035. [7] C. 1899, I. 176.

Of these hydrocarbons, cyclo-hexane (B. **28,** 1234; A. **302,** 2), methyl-, 1, 3-dimethyl-, 1, 3, 4-trimethyl-, and 1, 3, 5-dimethyl-ethyl-cyclo-hexane have been found in the naphtha of Caucasian petroleum, while methyl-, propyl-, 1, 3-dimethyl-, and 1, 4-methyl-iso-propyl-cyclo-hexane have been found in resin oil. Most of these have also been prepared by reduction of the corresponding benzene derivatives by the methods above named.

Cyclo-hexane, *hexahydro-benzol, naphthene, hexamethylene*

$CH_2\langle^{CH_2.CH_2}_{CH_2.CH_2}\rangle CH_2$, results from the reduction of benzene or of iodo-cyclo-hexane (see above); or by the action of sodium upon synthetic hexamethylene bromide. Pure hexamethylene is a liquid smelling like benzine. Heated with bromine to 150°, it yields sym. tetrabromo-benzol; digesting with nitric acid oxidises it to adipinic acid (A. **324**, 3).

Methyl-cyclo-hexane, *hexahydro-toluol, heptanaphthene,* has also been made from suberyl alcohol by the action of HI at 140° (B. **25**, R. 858), as well as from synthetic methyl-hexamethylene-ketone by means of the corresponding alcohol (B. **29**, 731). Bromine and aluminium bromide convert it into *pentabromo-toluol,* melting at 282°.

1, 3-Dimethyl-cyclo-hexane, *hexahydro-m-xylol, octonaphthene,* is obtained from camphoric acid, from heptanaphthene-carboxylic acid by means of HI (A. **225**, 110; B. **24**, 2718; **25**, 920; C. 1905, I. 1392), and from 2, 6-dimethyl-cyclo-hexanol; this substance has been obtained from optically active 1, 3-dimethyl-cyclo-hexanol, in a feebly dextro-rotatory form, $[\alpha]_D = 0{\cdot}8°$ (B. **35**, 2680). **1, 4-Dimethyl-cyclo-hexane** has been obtained synthetically from dimethyl-succinylo-succinic ester (B. **31**, 3206).

1, 3, 4-Trimethyl-cyclo-hexane, *hexahydro-pseudo-cumol, nononaphthene,* from 2, 3, 6-trimethyl-cyclo-hexanol (B. **29**, 215); when acted upon with bromine and aluminium bromide, it yields tribromo-pseudo-cumol.

n-Propyl-cyclo-hexane has also been formed from chloro-cyclo-hexane, propyl iodide, and zinc.

1, 3-Methyl-iso-propyl-cyclo-hexane, *sym. menthane,* b.p. 167°, is formed by the reduction of its iodine substitution product.

[1, 3]-Diethyl-cyclo-hexane, b.p. 170°, sp. gr. 0·7957 (22°), from 2, 6-diethyl-cyclo-hexanol.

Halogen Substitution Products of the Hexahydro-benzols.—Formation:—(1) From the hexahydro-benzols by the introduction of chlorine. (2) By the addition of halogens and halogen hydrides to di- and tetra-hydro-benzols. (3) By the addition of halogens to benzols and halogen benzols. (4) From cyclo-hexanols through the exchange of hydroxyl groups for halogens, by means of H haloids or P haloids.

The third method has brought to light some peculiar isomeric phenomena. *Two* isomeric benzene hexachlorides, and *two* isomeric chloro-benzol hexachlorides, have been found. The disposition on the part of chemists is to ascribe the cause of this isomerism to the different positions of the attached chlorine atoms with reference to the plane of the carbon ring, as in the case of the isomeric trithio-aldehydes and the isomeric tri-, tetra-, and pentamethylene-dicarboxylic acids.

Of the dihalogen cyclo-hexanes and the monohalogen alkyl-cyclo-hexanes, cis-trans- isomeric forms have also been discovered:

Chloro-cyclo-hexane	b.p. 143° [1]	**1, 2-Dichloro-cyclo-hexane**	b.p. 190°
Bromo-cyclo-hexane	,, 163° [2]	**1, 2-Dibromo-cyclo-hexane**	b.p.$_{100}$ 146°
Iodo-cyclo-hexane	b.p.$_{10}$ 69° [2]	**1, 4-Dibromo-cyclo-hexane**	m.p. 113° [5]
1, 1-Methyl-chloro-cyclo-hexane	b.p.$_{40}$ 54° [4]	**1, 4-Di-iodo-cyclo-hexane**	,, 145° [5]
1, 2-Methyl-chloro-cyclo-hexane	b.p. 156° [4]	**Hexahydro-benzyl chloride**	b.p.$_{100}$ 98° [6]
1, 3-Methyl-chloro-cyclo-hexane	,, 160° [4]	**Hexahydro-benzyl iodide**	b.p.$_{22}$ 103°.[7]
1, 4-Methyl-chloro-cyclo-hexane	,, 158° [4]		

Literature.—[1] C. 1898, I. 1294. [2] C. 1905, II. 1429. [3] A. **308**, 11; B. **34**, 2801. [4] C. 1905, I. 1242; B. **40**, 2062. [5] A. **278**, 94. [6] B. **40**, 2067. [7] B. **40**, 4865.

Various di-, tri-, and tetrachloro-cyclo-hexanes have been obtained, besides monochloro-cyclo-hexane, by the chlorination of cyclo-hexane at 0°. With KHO they yield cyclo-hexane, chloro-cyclo-hexane, chloro-hexadiene, benzene, and chloro-benzol (C. 1903, II. 664).

The halogen derivatives of the cyclo-hexanes cannot, like the aliphatic halogen alkyls, be converted into the corresponding alcohols, cyanides, mercaptans, etc., by transformation with alkali salts, and other substances of basic reaction like KCN, KSH, Ag_2O, NH_3, sodium-malonic ester, etc. Instead, they split off halogen hydride and form tetra- or dihydro-benzols. On the other hand, the cyclo-hexyl magnesium haloids are easily formed, and from these we may obtain, with oxygen, cyclo-hexanols; with CO_2, the cyclo-hexane-carboxylic acids; with aldehydes and ketones, extra-cyclic alcohols.

α- or **trans-Benzene hexachloride** $C_6H_6Cl_6$, melting at 157° and boiling at 218° (345 mm.), decomposes into 3HCl and unsym. trichloro-benzol. β- or **cis-Benzene hexachloride** melts and sublimes near 310°. α-Benzene hexachloride was made by the action of chlorine upon benzene in sunlight (1825, Faraday; 1835, Mitscherlich, *Pogg. A.* **35,** 370). α- and *β-Benzene hexachlorides* are produced when chlorine is conducted into boiling benzene (1884, Meunier; B. **18,** R. 149; **19,** R. 348), or, better, into a mixture of benzene and 1 per cent. sodium hydroxide. The α-body is separated by distillation in steam from the less volatile β-derivative (B. **24,** R. 632), or by means of chloroform from the more sparingly soluble β-compound. The latter is the more resistant of the two modifications. When heated with alcoholic potash it is converted with greater difficulty than the α-body into unsym. trichloro-benzol. It is not affected by alcoholic potassium cyanide, but, when boiled with this reagent, the α-variety is converted into unsym. trichloro-benzol. Zinc in alcoholic solution changes the α-modification into benzene (*Z. f. Ch.* 1871, N.F. **7,** 284, 293).

α- and **β-Chloro-benzol hexachloride** $C_6H_5Cl_7$, melting at 146° and 260°, yield 1, 2, 3, 5-tetrachloro-benzol with alcoholic potash (A. **141,** 101; B. **25,** 373). **1, 2, 4-Trichloro-benzol hexachloride** $C_6H_3Cl_9$ melts at 95°.

o-Xylol hexachloride $C_6H_4(CH_3)_2Cl_6$, m.p. 194°, b.p. 260°–265° (C. 1898, I. 1019).

α-Benzene hexabromide $C_6H_6Br_6$, melting at 212°, results from the action of bromine upon benzene in sunlight, and when bromine acts upon boiling benzene. When it splits off HBr, 1, 2, 4-tribromo-benzol is formed (*Pogg. A.* **35,** 374). It is isomorphic with α-benzene hexachloride (B. **18,** R. 553).

(1*b*) Cyclo-hexenes, Tetrahydro-benzols, Naphthylenes.

Tetrahydro-toluol has been found together with hexahydro-toluols and allied hydrocarbons in the essence of resin.

Cyclo-hexenes are produced artificially (1) from the halogen cyclo-hexanes by withdrawing the hydrogen haloid by means of alkali or tertiary amines, especially quinolin. (2) From amido-cyclo-hexanes, by dry distillation of their chlorohydrates or phosphates. (3) From the cyclo-hexanols by extracting water by means of SO_4HK, P_2O_5, $ZnCl_2$, $AlCl_3$, or by heating with aqueous oxalic acid (B. **34,** 3249),

or phthalic anhydride. In order to avoid possible transpositions during the extraction of water from cyclo-hexanols, these are transformed by the action of CS_2 upon their sodium or potassium salts, and by methylation of the resulting xanthogenates into the corresponding xanthogenic methyl esters, which, on distillation at ordinary pressure, decompose into COS, mercaptan, and the corresponding cyclo-hexene :

$$C_nH_{2n-1}O.CS.SCH_3 = C_nH_{2n-2}+COS+CH_3SH.$$

This method is particularly suitable for the higher molecular alcohols, and has been very serviceable for preparing terpenes. Those alkylidene-cyclo-hexanes which contain a semi-cyclic linkage are isomeric with alkyl-cyclo-hexenes (compare ethylidene-cyclo-hexane, etc.). These hydrocarbons, which are of special importance in the chemistry of terpenes, are generated by discarding CO_2 from the cyclo-hexene and cyclo-hexylidene fatty acids obtained by condensation of cyclo-hexanones with bromo-aliphatic esters and zinc, with dehydration. They differ from the isomeric cyclo-hexenes, with unsaturated rings, by their higher specific gravities, higher boiling-points, and abnormal molecular refraction (A. **360**, 36). On heating with alcoholic sulphuric acid, they easily shift the double linkage and become true tetrahydro-benzols. A similar capacity for transposing into hydrocarbons of the same linkage, especially under the influence of acids, is shown, to some extent, by all alkyl-cyclo-hexenes, so that the preparation of a perfectly uniform hydrocarbon, apart from cyclo-hexene itself, has probably not yet been accomplished. Characteristic of the cyclo-hexenes are their addition products with NOCl, N_2O_3 and N_2O_4, the so-called nitroso-chlorides, nitrosites, and nitrosates (compare terpenes).

Cyclo-hexene, tetrahydro-benzol $CH_2\langle\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}\rangle CH$, boiling at 82°–84°, is produced on distilling monobromo- and monochloro-cyclo-hexane with quinolin or alcoholic potash (A. **302**, 27), and from cyclo-hexanol by heating with oxalic acid (B. **34**, 3252) or $HKSO_4$ (C. 1905, I. 1014). It is a colourless liquid, resembling petroleum. It has less of the leek odour than dihydro-benzol. It is coloured yellow by concentrated sulphuric acid.

With ozone it yields a very stable *ozonide* $C_6H_{10}O_3$, which can be recrystallised from alcohol, m.p. 75°. Water decomposes this, with formation of adipin-dialdehyde and adipinic acid (B. **42**, 694). The *nitroso-chloride* melts at 152°. The *nitrosate* $NO.C_6H_{10}.O.NO_2$ melts at 150° with decomposition (A. **343**, 49).

Methyl-cyclo-hexenes, tetrahydro-toluols $C_6H_9.CH_3$. Three methyl-cyclo-hexenes are possible, isomeric by the position of the double linkage. The most stable of these is—

Δ^1-Methyl-cyclo-hexene * $CH_3C\langle\begin{matrix}CH—CH_2\\CH_2—CH_2\end{matrix}\rangle CH_2$, b.p. 106°–108°, D_{17} 0·799. The isomeric hydrocarbons easily pass into this substance, with displacement of the double linkage. It is formed, nearly pure,

* Δ^1, Δ^2, Δ^3, etc. indicates the situation of a double linkage of the C-atom 1, 2, 3, etc. reckoned with reference to the next higher number. It is sometimes preferable to affix the number indicating the double linkage to the name, *e.g.* "methyl-cyclo-hexene-1." The same notation is sometimes used to indicate the position of the hydroxyl or keto-group in the alcohols and ketones, *e.g.* "1-methyl-cyclo-hexanone-3."

from 1, 1- and 1, 2-methyl-cyclo-hexanol. It is formed, practically pure, from 1, 1- and 1, 2-methyl-cyclo-hexanol by elimination of water (see also A. **359**, 287). An apparently fairly uniform Δ^3-**methyl-cyclo-hexene**, b.p. 103°, D_{15} 0·841, $[\alpha]_D$+110°, has been obtained by heating acid phthalic ester, or the methyl-xanthogenate of the optically active 1, 3-methyl-cyclo-hexanol. On oxidation with $KMnO_4$, it yields β-methyl-adipinic acid (C. 1904, I. 1346, 1213). Δ^2-**Methyl-cyclo-hexene**, b.p. 103°, D_{27} 0·7937, $[\alpha]_D$+81·47°, from 1, 3-methyl-iodo-cyclo-hexane (B. **34**, 3252; **35**, 2493).

Synthetically, a methyl-cyclo-hexene has been obtained from perseite (Vol. I.) by heating with HI (B. **25**, R. 503).

Isomeric with the tetrahydro-toluols is **methene-cyclo-hexane** $CH_2:C\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle CH_2$, b.p. 106°, D_{20} 0·8020, n_D=1·4516, from cyclo-hexene-acetic acid, and from hexahydro-benzyl iodide, with alcoholic potash (A. **359**, 291; B. **40**, 4863). It yields, on oxidation with $KMnO_4$, besides cyclo-hexanone, a *glycol* $C_7H_{12}(OH)_2$, m.p. 77°, which, on heating with dilute H_2SO_4, passes into hexahydro-benzaldehyde. On boiling with alcoholic sulphuric acid, it is transposed into Δ^1-methyl-cyclo-hexene. Nitrole-piperidide, m.p. 127°.

Several homologous tetrahydro-benzols have been obtained, mostly by elimination of water from the corresponding cyclo-hexanols. As regards their uniformity the above remarks apply.

1, 2-Dimethyl-cyclo-hexene, b.p. 132°, is formed from the 2, 2-dimethyl-cyclo-hexanol, by dehydration and migration of a methyl group (reversal of the pinacolin transposition, see Vol. I.); it easily yields crystalline dibromide melting at about 138° (private communication of H. Meerwein). **1, 3-Dimethyl-cyclo-hexene**, b.p. 124°. **1,4-Dimethyl-cyclo-hexene-1** (B. **41**, 2632). **1, 1-Dimethyl-cyclo-hexene**, b.p. 117°, from **dimethyl-dihydro-resorcin**, yields, on oxidation by $KMnO_4$, a mixture of α, α- and β, β-dimethyl-adipinic acid (C. 1907, I. 239). Δ^1-**ethyl-**, **propyl-**, and **iso-propyl-cyclo-hexenes** boil at 135°, 155°, and 156° respectively; they are formed by linkage displacements from ethylidene-, propylidene-, and **iso-propylidene-cyclo-hexane**, b.p. 138°, 158°, and 161° (A. **360**, 44). **Allyl-cyclo-hexane** $C_6H_{11}.CH_2.CH:CH_2$, b.p. 149°, from cyclo-hexyl-magnesium bromide and **allyl bromide** (C. 1910, II. 387). α-**Cyclo-geraniolene**, 1, 3, 3-*trimethyl-cyclo-hexene*-5 $CH_2C.CH_2.C(CH_3)_2$ $CH.CH_2.CH_2$, b.p. 139°–141°, is formed, besides the isomeric β-cyclo-geraniolene, from the olefinic terpene *geraniolene* by treating with sulphuric acid. It is also formed from the *synthetic dimethyl-heptinol* $(CH_3)_2C(OH).CH_2.CH_2.CH:C(CH_3)_2$ by boiling with phosphoric acid (B. **37**, 848), and by the action of zinc chloride upon dihydro-iso-aceto-phorol or 3, 5, 5-trimethyl-cyclo-hexanols, it yields a sparsely soluble nitroso-chloride and nitrosate (A. **324**, 97, 112).

Special interest attaches to Δ^1- and Δ^3-1, 4-methyl-iso-propyl-cyclo-hexene, the so-called *carro-menthene* and *menthene*, which are closely related to the terpenes, and are therefore treated among hydro-terpenes.

(1*c*) Dihydro-benzols [Cyclo-hexadienes].

Very probably some of the naturally occurring terpenes belong to the dihydro-benzols. The artificially prepared representatives of the di-

hydro-benzols are very similar in behaviour to them. The method of preparing the simplest of the hydrocarbons in this class—dihydro-benzol—from succino-succinic ester has already been discussed. Mono-alkyl and di-p-alkyl-dihydro-benzols were made in like manner from mono- and di-alkyl-succino-succinic esters (B. **26**, 232).

The other methods of preparing dihydro-benzols are quite analogous to this for cyclo-hexenes. They are formed (1) from the cyclo-hexane diols which are obtained mostly by reduction of the easily synthesised dihydro-resorcins as well as from cyclo-hexenols by dehydration; (2) from the dibromides of the cyclo-hexenes by heating with quinolin (compare B. **42**, 693); (3) by distillation of the phosphates of diamido-cyclo-hexanes in a stream of CO_2, if necessary under diminished pressure (A. **328**, 88; C. 1909, II. 356).

The dihydro-benzols mostly have a penetrating odour like that of leeks. They are easily polymerised and resinified. With alcoholic sulphuric acid and aceto-anhydride and sulphuric acid, they give characteristic red or purple colours. By oxidising agents they can usually be easily transformed into benzene derivatives.

The situation of the double linkages, and especially their uniformity, is in most cases more doubtful in the dihydro-benzols than it is even in the tetrahydro-benzols. The physical data communicated therefore only apply to a mixture of hydrocarbons which, according to its transformations, consists mostly of the cyclo-hexadiene in question. On the utilisation of molecular refraction for determining the constitution of dihydro-benzols, see B. **43**, 3076.

$\Delta^{1,3}$-Cyclo-hexadiene, dihydro-benzol $CH\langle\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}\rangle CH$, b.p. 81·5°, from 1, 3-diamido-hexamethylene phosphate by distillation, from 1, 3-dichloro- and 1, 2-dibromo-cyclo-hexane by heating with quinolin besides some cyclo-hexene and small quantities of the isomeric **$\Delta^{1,4}$-dihydro-benzol** $CH\langle\begin{matrix}CH—CH_2\\CH_2—CH\end{matrix}\rangle CH$, b.p. 81·5°, which is the chief product formed from 1, 4-diamido-cyclo-hexane. The 1, 4-cyclo-hexadiene easily yields a tetrabromide, m.p. 188°, whereas the 1, 3-cyclo-hexadiene yields chiefly a dibromide, m.p. 109°, probably 1, 4-dibromo-Δ^2-cyclo-hexene, which, on heating with quinolin, becomes benzene. The dihydro-benzol formed from 1, 4-dibromo-hexamethylene is a mixture of both isomers (A. **328**, 105; B. **41**, 2479; **42**, 693; C. 1904, II. 1736).

$\Delta^{1,3}$-Dihydro-toluol $C_6H_7.CH_3$, b.p. 111°, from m-diamido-hexahydro-toluol phosphate, on oxidation with $KMnO_4$ gives methyl-dioxy-hexamethylene-ketone or methyl-cyclo-hexanone-diol, and then succinic and oxalic acids, which determine its constitution. But this hydrocarbon also lacks uniformity (B. **41**, 1698). **$\Delta^{3,4}$-Dihydro-toluol**, b.p. 106°, D_{20} 0·8274 (B. **41**, 2484). **$\Delta^{3,6}$-Dihydro-toluol**, b.p. 109°, D_{20} 0·8292 (B. **41**, 2630).

1, 1-Dimethyl-cyclo-hexadiene (see B. **36**, 2692; C. 1909, II. 356).

Dihydro-o-xylol, *cantharene*, b.p. 135°, is produced when cantharic acid $C_{10}H_{12}O_4$, a rearrangement product of cantharidin, is distilled with caustic lime. Its odour is like that of a terpene, and it resinifies on exposure to the air (Piccard, 1878; B. **25**, 2453; A. **328**, 115).

$\Delta^{3,5}$-Dihydro-m-xylol, b.p. 129°, D_{18} 0·8203, from **3, 5-diamido-1, 3-dimethyl-cyclo-hexane** and from **1, 3-dimethyl-5-chloro-cyclo-**

hexadiene-3, 5, the product of the action of PCl_5 upon 1, 3-dimethyl-cyclo-hexenone, by reduction (B. **48,** 3111).

$\Delta^{2,4}$-Dihydro-m-xylol, b.p. 129°, D_{20} 0·8225 (see B. **41,** 2631). A mixture of hydrocarbons containing a dihydro-m-xylol, besides m-xylol and tetrahydro-m-xylol, has been obtained from methyl-heptenone $(CH_3)_2C:CH.CH_2.CH_2COCH_3$ by condensation with $ZnCl_2$ (C. 1909, II. 357).

$\Delta^{1,3}$-Dihydro-p-xylol, b.p. 135°–138°, D_{19} 0·8314, has been obtained by a peculiar reaction on boiling dichloro-α, β-pulenenone with alcoholic potash; it polymerises easily. Oxidation with $KMnO_4$ produces acetyl-acetone, which proves its constitution (B. **41,** 1816; **42,** 2404). **$\Delta^{3,4}$-Dihydro-p-xylol,** b.p. 133° (B. **41,** 2633). **Dihydro-p-diethyl-benzol,** b.p. 180°–185°.

Addendum: Cyclo-hexyl-acetylenes.—While steric conditions militate against the possibility, or at least the stability, of combinations of cyclo-hexane with an acetylene binding in the nucleus, as well as of combinations with two double linkages in the allene position, cyclo-hexyl-acetylenes with the acetylene binding in the side chain have been obtained by the methods usual in aliphatic series.

Cyclo-hexyl-acetylene $C_6H_{11}C:CH$, b.p. 131°, from cyclo-hexyl-chlor-ethylene with KHO; it gives a Na salt, which with CO_2 forms hexahydro-phenyl-propiolic acid (C. 1909, II. 2081). **Cyclo-hexyl-allylene** $C_6H_{11}CH_2.C:CH$, b.p. 165°–170° (see C. 1910, II. 387).

(*2a*) Ring-alcohols of the Hydro-aromatic Carbons.

In this group are included quercite and inosite, formerly classed with the sugars, as well as the ring-alcohols of the terpane or menthane group among the terpenes, while other members have been obtained by the reduction of aromatic or hydro-aromatic compounds, but chiefly from the corresponding ketones, which yield, by reduction, secondary ring-alcohols, and, by transformation with magnesium-alkyl-iodides (Vol. I.), tertiary ring-alcohols (B. **34,** 2877; *Ann. Chim. Phys.*, 8, **10,** 527). Cyclo-hexanols have also been obtained by the action of oxygen upon cyclo-hexyl-magnesium haloids, from the ring amines with HNO_2, by the attachment of water to cyclo-hexenes, by heating with glacial acetic acid and concentrated H_2SO_4. Many alkyl-cyclo-hexanols occur in stereo-isomeric forms.

Name.	M.p.	B.p.	D.	
Cyclo-hexanol	15°	160°	0·9471 (22°)	
1-Methyl-cyclo-hexanol	12°	157°	0·9387 (12°)	B. **34,** 2880; C. 1904, II. 219
2-Methyl-cyclo-hexanol	..	165°	0·936 (14°)	C. 1909, I. 850
3-Methyl-cyclo-hexanol	..	172°	0·926 (12°)	C. 1905, I. 742
4-Methyl-cyclo-hexanol	..	174°	0·924 (14°)	C. 1905, I. 742
1-Ethyl-cyclo-hexanol	33°	166°	..	C. 1904, II. 219
1, 2-Dimethyl-cyclo-hexanol	..	166°	0·926 (14°)	C. 1905, II. 483
1, 3-Dimethyl-cyclo-hexanol	..	169°	0·911 (14°)	C. 1907, I. 1606
1, 4-Dimethyl-cyclo-hexanol	50°	170°	..	C. 1906, I. 1096
2, 2-Dimethyl-cyclo-hexanol	6·5°	63° (18 mm.)	..	..
2, 4-Dimethyl-cyclo-hexanol	..	179°	0·9073 (16°)	C. 1906, I. 1248
2, 5-Dimethyl-cyclo-hexanol	..	..	0·9073 (16°)	C. 1906, I. 1248
2, 6-Dimethyl-cyclo-hexanol	..	174·5°	..	B. **28,** 781
3, 3-Dimethyl-cyclo-hexanol	12°	78° (15 mm.)	0·9129 (15°)	C. 1907, I. 964
3, 5-Dimethyl-cyclo-hexanol	..	189°	0·9119 (16°)	C. 1906, I. 1248
3, 5-Dimethyl-cyclo-hexanol	..	187°	0·9019 (16°)	A. **207,** 160

Cyclo-hexanol, *hexahydro-phenol* $CH_2\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle CHOH$ is formed (1) from cyclo-hexanone by reduction with sodium and aqueous ether (B. **34,** 2800); (2) from p-iodo-hexahydro-phenol, the product of the action of HI upon quinite, by reduction with zinc dust and glacial acetic acid; (3) from amido-hexamethylene and from pentamethylene-methyl-amine with nitrous acid (A. **302,** 20); (4) by passing gaseous phenol and hydrogen over reduced nickel at about 170° (C. 1904, I. 454, 727; 1905, I. 1243); (5) by the action of oxygen upon cyclo-hexyl-magnesium chloride (C. 1907, I. 1695). It smells like fusel-oil, and is more soluble in water than the aliphatic alcohols with 6 C atoms (B. **26,** 229). Its acetyl compound melts at 104°. With HBr it forms a bromo-cyclo-hexane. On oxidation with nitric acid (density 1·2), or $KMnO_4$, it gives a good yield of adipinic acid (for method of preparing this acid, see B. **41,** 575; C. 1908, I. 1835). **Cyclo-hexanol-methyl ether** $C_6H_{11}OCH_3$, b.p. 135°·5, from sodium-cyclo-hexanol and ICH_3, or by reduction of anisol with hydrogen and nickel. For the ester of cyclo-hexanol, see C. 1905, I. 1014. **Cyclo-hexyl ether** $C_6H_{11}.O.C_6H_{11}$, b.p. 276°, from diphenyl ether with hydrogen and nickel (B. **41,** 1001).

3-Methyl-cyclo-hexanol has also been obtained in its lævo-rotatory form $[\alpha]_D=-3°\ 40'$ by reduction of the optically active 3-methyl-cyclo-hexanone (B. **30,** 1534).

1-Methyl-cyclo-hexanol is produced by nuclear synthesis in the action of 1, 5-magnesium-dibromo-pentane upon acetic ester (C. 1907, II. 681).

3-Methyl-6-propyl, 3-methyl-6-iso-butyl-, and **3-methyl-6-iso-amyl-cyclo-hexanol,** b.p.$_{22}$ 112°, m.p. 69°, and b.p.$_{23}$ 137° respectively, are obtained synthetically by heating 3-methyl-cyclo-hexanone with sodium and propyl-iso-butyl- and iso-amyl-alcohol to about 220° (C. 1905, I. 872, 1100). **3, 6, 6-Trimethyl-cyclo-hexanol,** "*pulenol,*" b.p. 188° (see A. **329,** 87).

Hexahydro-thymol and **hexahydro-carvacrol** (see Menthol and Carvomenthol).

Polyvalent Ring-alcohols are produced (1) by reduction of poly-keto-cyclo-hexanes; (2) from polyvalent phenols, by reduction with hydrogen and nickel (C. 1908, II. 240); (3) from cyclo-hexenes by gentle oxidation with $KMnO_4$, or by transformation of the corresponding halogen hydrins.

trans-Cyclo-hexane-1, 2-diol, *o-dioxy-hexahydro-benzol* $C_6H_{10}[1, 2](OH)_2$, m.p. 100°, b.p. 225°, is obtained from tetrahydro-benzol with $KMnO_4$ (A. **302,** 21) or by reduction of pyro-catechin. The *isomeric cis-*1, 2-*cyclo-hexane-diol,* m.p. 104°, b.p. 236°, is produced from the iodo-hydrin, *o-iodo-cyclo-hexanol* $C_6H_{10}I(OH)$, m.p. 42°, obtained from cyclo-hexene with iodine and mercury, and yielding, with silver oxide and KHO, at first a cyclo-hexene oxide $C_6H_{10}>O$, b.p. 131°, resembling ethylene oxide. This combines with water to form cis-cyclo-hexane-diol, with bisulphite to cyclo-hexanol-sulphonic acid $C_6H_{10}(OH)SO_3H$, with ammonia to o-amino-cyclo-hexanol $C_6H_{10}[1, 2](NH_2)(OH)$, m.p. 66°, b.p. 219° (C. 1905, II. 1337).

1-Methyl-cyclo-hexane-1, 2-diol, m.p. 67°, from Δ^1-methyl-cyclo-hexene; on heating with oxalic acid it yields 1, 2-methyl-cyclo-hexanone.

4-Methyl-cyclo-hexene-1, 2-oxide, b.p. 146°, from the chloro hydrin of Δ^3-methyl-cyclo-hexene with KOH (A. **336,** 310).

Cyclo-hexane-1, 3-diol, m.p. 65°, by reduction of resorcin with H and Ni at 130° (C. 1908, II. 240).

Quinite [*Cyclo-hexane-1, 4-diol*] $HOCH\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle CHOH$, m.p. 144°, is formed from p-diketo-hexamethylene, when treated with sodium amalgam, in the presence of carbon dioxide, or by reducing hydroquinone with H and Ni. This was demonstrated by A. v. Baeyer in 1892. It tastes sweet at first, then bitter, and is readily soluble in water and in alcohol. Chromic acid oxidises it to quinone (B. **25,** 1038; **34,** 506). Quinite serves for the preparation of the simple hydride derivatives of benzene (B. **26,** 229). Hydriodic acid converts it into **p-iodo-cyclo-hexanol** and **p-di-iodo-cyclo-hexane.** By reduction the first yields hexahydro-phenol, the second cyclo-hexane. **p-Dibromo-cyclo-hexane** passes readily into **dihydro-benzol** (B. **26,** 230). **2, 5-Dimethyl-quinite** is formed from the corresponding diketone (B. **25,** 2122).

Phloro-glucite, s-trioxy-hexamethylene, cyclo-hexane-1, 3, 5-triol $HOCH\langle\begin{matrix}CH_2—CH(OH)\\CH_2—CH(OH)\end{matrix}\rangle CH_2 + 2H_2O$, melts when anhydrous at 184°. It is formed when phloro-glucin is reduced in an approximately neutral solution with sodium amalgam (B. **27,** 357).

Cyclo-hexane-1, 2, 3-triol, α-form, m.p. 108°; β-form, m.p. 124°, from Δ^2-ethoxy-cyclo-hexene with $KMnO_4$, and saponification of the resulting ethoxy-cyclo-hexane-diol with concentrated HBr (C. 1910, I. 2017).

Quercite, *cyclo-hexane-pentol* $CH_2\langle\begin{matrix}CH(OH)—CH(OH)\\CH(OH)—CH(OH)\end{matrix}\rangle CH(OH)$, m.p. 235°, $[\alpha]_D = +24{\cdot}16°$, occurs in acorns. The aqueous extract of the latter can be freed of glucoses by fermentation with beer-yeast. Also from the leaves of *Chamærops humilis* (C. 1908, I. 267). Quercite does not ferment with yeast. Hydriodic acid converts it into benzene, hexane, phenol, quinone, and hydroquinone (Prunier). Nitric acid oxidises it to mucic acid and trioxy-glutaric acid (see Vol. I.). A solution of potassium permanganate converts it chiefly into malonic acid, although oxalic acid and carbonic acid are formed simultaneously (B. **29,** 1762). A lævo-rotatory quercite, m.p. (anhydrous) 174°, $[\alpha]_D = -73{\cdot}9°$, has been discovered in the leaves of *Gymnema silvestre.* Penta-acetyl compound, m.p. 125° (C. 1904, II. 329).

Inosite, *hexahydro-hexaoxy-benzol, cyclo-hexane-hexene* $C_6H_6(OH)_6$, has seven possible optically inactive, and two optically active, modifications, as well as a racemic form (cp. Vol. I.). The only modifications known with certainty are one inactive and two active forms, and the racemic form.

i-Inosite, *phaseomannite, dambose* $C_6H_6(OH)_6 + 2H_2O$, melts at 225° when anhydrous. It occurs in the muscles of the heart and in the urine when there has been an excessive consumption of water; also in unripe beans (*Phaseolus vulgaris*) and peas. If heated to 170° with hydriodic acid, it yields phenol, di-iodo-phenol, and traces of benzene (Maquenne). Concentrated nitric acid oxidises it to di- and tetra-oxy-quinones, and to rhodizonic acid (B. **20,** R. 478; **23,** R. 26; C. 1908, I. 269). It yields furfurol on heating with P_2O_5 (C. 1908, I. 2152).

Dambonite $C_6H_6(OH)_4(OCH_3)_2+3H_2O$ is the dimethyl ether of i-inosite. It occurs in the rubber from *Gabon*. **i-Inosite hexa-acetate** melts at 211°.

d-Inosite, melting at 247°, $[\alpha]_D=+65°$, from pinite by the action of hydriodic acid, behaves like i-inosite with nitric acid. **Pinite,** *matezite* $C_6H_6(OH)_5(OCH_3)$, melting at 186°, $[\alpha]_D=+65{\cdot}51°$, is present in the juice of *Pinus Lambertiana*, also in the rubber from *Mateza roritina* of Madagascar.

l-Inosite, melting at 238°, $[\alpha]_D=-55°$, from quebrachite by means of hydriodic acid, behaves towards nitric acid just like i-inosite. **Quebrachite** $C_6H_6(OH)_5OCH_3$, melting at 186°, $[\alpha]^D=-80°$, occurs in the quebracho bark. Racemic inosite melts at 253°.

Scyllite $C_6H_{12}O_6$, m.p. about 340°, probably a second inactive inosite, was discovered by Staedeler in 1856. It is found in the organs of various plagiostomes, *e.g. Scyllium canicula*, but most plentifully in the kidneys of roach and pike (?), from which it is separated by means of its slightly soluble lead salt (B. **40,** 1821).

Cocosate $C_6H_{12}O_6$, m.p. 345°–350°, from the leaves of *Cocos nucifera* and *Cocos plumosa*, is very similar to inosite in its behaviour, and is oxidised, like the latter, to rhodizonic acid by H_2O_2. The hexa-acetyl compound melts about 300° (C. 1908, I. 267).

Phenose $C_6H_6(OH_6)$ (?) is an amorphous, readily soluble substance, deliquescing in the air. It has a sweet taste and reduces Fehling's solution, but is not capable of fermentation. It has been obtained by the action of a soda solution (A. **186,** 323) upon the addition product of benzene with three molecules of hypochlorous acid $C_6H_6\{^{Cl_2}_{(OH)_2}$.

(2*b*) Ring Alcohols of Tetrahydro-benzol.

Δ^3-Cyclo-hexanol, *tetrahydro-phenol* $CH\langle^{CH\,—\,CH_2}_{CH_2—\,CH_2}\rangle CHOH$, b.p. 163°, is formed when p-iodo-cyclo-hexanol is distilled with quinolin.

Δ^2-Cyclo-hexanol-methyl and **ethyl ether** C_6H_9OAlk, b.p. 139° and 154° respectively, from the methyl and ethyl iodo-hydrins of cyclo-hexane, the results of the action of iodine and HgO upon an alcoholic solution of cyclo-hexene, by boiling with alcoholic potash. From the corresponding dibromides we obtain, by saponification and reduction with zinc dust and alcohol, **Δ^2-cyclo-hexenol** $CH_2\langle^{CH=CH}_{CH_2—\,CH_2}\rangle CHOH$, b.p. 165° with decomposition. The urethane melts at 108° (C. 1905, II. 1339); the Δ^1-cyclo-hexenol acetate, b.p. 180°–182°, is formed by heating cyclo-hexanone with acetic anhydride and sodium acetate (B. **41,** 564).

Numerous Δ^2-cyclo-hexenols have been obtained by reduction of the 3-alkyl-Δ^2-cyclo-hexenones, *e.g.* **3-methyl-Δ^2-cyclo-hexenol,** b.p. 176° (A. **289,** 131).

Dihydro-cumin alcohol $C_9H_{13}.CH_2OH$, b.p.$_5$ 93°, has been found in ginger grass and peppermint (?) oil (B. **44,** 466). It is also produced from α-phellandrene-glycol, on heating with dilute H_2SO_4.

(2*c*) Extra-cyclic Hydro-aromatic Alcohols.

These have been obtained (1) by transformation of cyclo-hexyl-magnesium haloids with aldehydes and ketones; (2) from cyclo-

hexane-carbocyclic esters, and extra-cyclic hydro-aromatic ketones by reduction, or by the action of alkyl-magnesium haloids; (3) by oxidation of alkylidene-cyclo-hexanes with dilute permanganate:

Cyclo-hexyl-carbinol	$C_6H_{11}.CH_2OH$	b.p. 181°	D_0 0·944	C. 1904, II. 704.
Cyclo-hexyl-methyl-carbinol	$C_6H_{11}.CH(OH)CH_3$	,, 189°	D_0 0·946	C. 1907, I. 1695.
Cyclo-hexyl-dimethyl-carbinol	$C_6H_{11}C(OH)(CH_3)_2$	b.p.$_{20}$ 96°	D_0 0·938	B. **40**, 4165.
β-Cyclo-hexyl-ethyl-alcohol	$C_6H_{11}CH_2.CH_2OH$	b.p. 206°		B. **41**, 2628.

1-Methyl-cyclo-hexane-1, 7-diol $C_6H_{10}(OH).CH_2OH$, m.p. 77°, by oxidation of methylene-cyclo-hexane with $KMnO_4$; with acids it yields hexahydro-benzaldehydes (A. **347**, 331).

1-Iso-propyl-cyclo-hexane-1, 7-diol $C_6H_{10}(OH).C(OH)(CH_3)_2$, m.p. 83°, from 1, 1-cyclo-hexanol-carboxylic ester and CH_3MgI; on heating with dilute H_2SO_4 it undergoes pinacolin transposition and yields 1-methyl-1-acetyl-cyclo-hexane (C. 1910, II. 466).

(2*d*) Sulphur Derivatives of Hydro-aromatic Alcohols.

Cyclo-hexyl mercaptan, *hexahydro-thio-phenol* $C_6H_{11}SH$, b.p. 158°–160°, a colourless, highly refractive oil of penetrating odour of mercaptan, is obtained in small quantities by transformation of halogen-cyclo-hexanes with KSH; and, more easily, by splitting up cyclo-hexyl-xanthogenic ester $C_6H_{11}S.CSOC_2H_5$, b.p.$_{16}$ 152°, with ammonia. It is also prepared by the action of sulphur upon cyclo-hexyl-magnesium chloride (C. 1910, I. 1830), or by reduction of cyclo-hexane-sulphonic acid chloride, b.p.$_{15}$ 127°, with tin and HCl. It yields a sparingly soluble mercury salt. **Cyclo-hexyl-methyl sulphide** $C_6H_{11}S.CH_3$, b.p. 180°, from the Na salt with ICH_3. **Dicyclo-hexyl disulphide** $(C_6H_{11})_2S_2$, b.p. 288°, from the Na salt with iodine (B. **39**, 392; **40**, 2220).

(3*a*) Ring-amines of Hydro-aromatic Hydrocarbons.

These are formed (1) by reduction of nitro-hexahydro-benzols with zinc or tin and HCl, or of the oximes of the corresponding ketones with sodium in alcoholic solution; m-diamines, especially, have been obtained by reducing the hydroxylamine oximes, the addition products of hydroxylamine with cyclo-hexenone oximes; (2) by reduction of anilines with Ni and H (C. 1904, I. 884; B. **41**, 991); (3) by heating cyclo-hexanones with ammonium formate, or the formates of organic bases (A. **348**, 54); (4) from the cyclo-hexane-carboxylic amides by decomposition with bromine and alkali (B. **40**, 2061).

Amido-cyclo-hexane, *cyclo-hexylamine* $C_6H_{11}NH_2$, a strong base, boiling at 134°, smells of coniin; but slightly soluble in water. It is prepared from cyclo-hexanone oxime, or from the nitro-hexamethylene $C_6H_{11}NO_2$, b.p. 206°. On conducting aniline vapour with hydrogen over reduced nickel at 190°, we obtain—besides cyclo-hexyl-amine—**cyclo-hexyl-aniline** $C_6H_{11}NHC_6H_5$, b.p.$_{30}$ 71°, and **dicyclo-hexyl-amine** $(C_6H_{11})_2NH$, b.p.$_{30}$ 145° (C. 1904, I. 884). **Acetamido-cyclo-hexane,** m.p. 104°. Its benzol compound melts at 147°, and is also obtained by transposition of α-hexahydro-benzo-phenone oxime (*q.v.*) (B. **30**, 2863). Phenyl-urea derivative, m.p. 180°; phenyl-thio-urea derivative, m.p. 147° (A. **302**, 22). **Cyclo-hexyl-methyl-, -ethyl-,** and **-dimethyl-amine,** b.p. 145°, 164°, and 165°, are formed by hydrogenating the alkyl-anilines with H and Ni (C. 1904, II. 105).

1, 1-Amido-methyl-cyclo-hexane $C_6H_{10}(CH_3)NH_2$, b.p. 143°, from 1, 1-nitro-methyl-cyclo-hexane, b.p.$_{40}$ 110°, and by method 4 (C. 1910, II. 1377). Benzoyl compound, m.p. 101°.

1, 2-Amido-methyl-cyclo-hexane, b.p. 150°; benzoyl compound, m.p. 147°.

1, 3-Amido-methyl-cyclo-hexane, b.p. 152°; benzoyl compound, m.p. 163°, from methyl-cyclo-hexanone oxime, and from 1, 3-nitro-methyl-cyclo-hexane, b.p.$_{40}$ 120°, by reduction, is converted into **methyl-cyclo-hexyl-hydrazin** $C_6H_{10}(CH_3)NHNH_2$ by treating its bromyl compound with Ag_2O (C. 1900, I. 653).

1, 4-Amido-methyl-cyclo-hexane, b.p. 151°; benzoyl compound, m.p. 181°.

o-Diamido-cyclo-hexane $C_6H_{10}[1, 2](NH_2)_2$ is an oil, boiling at 183°–185°. It results when the amide of hexahydro-anthranilic acid is treated with sodium hypobromite and then with hydrochloric acid. Like the aromatic o-diamines, it unites with benzaldehydes, forming aldehydines (A. **295,** 187).

m-Diamido-cyclo-hexane, boiling at 193°, smells like ethylene-diamine. It is soluble in water. Nitrous acid decomposes it into nitrogen and dihydro-benzol (A. **228,** 39). The *diaceto-compound* melts at 256°.

p-Diamido-cyclo-hexane $C_6H_{10}[1, 4](NH_2)_2$ is a liquid (B. **27,** 1449).

m-Diamido-hexahydro-toluol $C_6H_9[1, 3, 3](CH_3)(NH_2)_2$, b.p.$_{17}$ 85°–89°, **m-diamido-hexahydro-xylol,** b.p.$_{27}$ 103°–105°, **m-diamido-hexahydro-m-cymol,** b.p.$_{10}$ 103°–105°, from the corresponding hydroxylamine oximes, **gem-dimethyl-3, 5-diamido-cyclo-hexane,** b.p.$_{10}$ 103°–105° (A. **328,** 105). Cp. also the ring amines of the terpane and menthane groups, discussed among the terpenes.

(3*b*) Extra-cyclic Hydro-aromatic Amines.

Cyclo-hexyl-methyl-amine, *hexahydro-benzyl-amine* $C_6H_{11}.CH_2NH_2$, b.p. 163°, benzoyl compound, m.p. 108°, from cyclo-hexyl-acetamide with sodium hypo-bromite, and by reduction of hexahydro-benzo-nitrile (A. **353,** 298). With HNO_2 it is partly transformed into suberyl-alcohol with ring expansion (A. **353,** 326).

β-Cyclo-hexyl-ethyl-amine $C_6H_{11}.CH_2.CH_2NH_2$, b.p. 188°, by reduction of cyclo-hexyl-aceto-nitrile (A. **353,** 297).

(4) Ring-ketones of the Hydro-aromatic Hydrocarbons.

(*a*) *Ring-ketones of Hexahydro-benzols.*—These belong to the most easily accessible hydro-aromatic substances, starting from which numerous other compounds can be prepared, and which have, therefore, been studied in detail.

Methods of Formation.—(1) By oxidation of the corresponding cyclo-hexanols with chromic acid, or by conducting their vapours over finely divided metallic copper at 300° (C. 1903, I. 1212). (2) From cyclo-hexene-glycols with dilute acids. (3) By nuclear synthesis from pimelinic acid and its alkyl substitution products by distillation of their calcium salts or anhydrides (C. 1907, II. 685). (4) From the synthetic cyclo-hexanone-carboxylic esters and their alkylation products by saponification and elimination of CO_2. (5) By the action of

$NaNH_2$ and halogen alkyl upon 1, 3-methyl-cyclo-hexanone; an H atom in the neighbourhood of CO can be replaced by alkyl (C. 1905, I. 605). (6) Several 1, 2-alkyl-cyclo-hexanones have been obtained from the Mg-compound of 1, 2-chloro-cyclo-hexanone by transposition with halogen alkylene (C. 1906, II. 126).

Behaviour.—(1) Like the aliphatic ketones, cyclo-hexanones combine with hydroxylamine, phenyl-hydrazin, semi-carbazide, prussic acid, etc., some also with sodium bisulphite. (2) Reduction with Na and moist ether produces cyclo-hexanols. (3) Sodium ethylate or gaseous HCl—they, like acetone, undergo self-condensation with combination of two or three molecules and elimination of water. (4) Cyclo-hexanones condense with benzaldehyde, forming characteristic mono- or dibenzyl compounds by joining up two methylenes adjoining the CO group (C. 1908, I. 638). (5) With acetic ester, and sodium, they form 1, 2-acetyl-cyclo-hexanones, with oxalic ester and sodium ethylate 1, 2-cyclo-hexanone-oxalic esters (A. **348**, 91), with $NaNH_2$ and CO_2 1, 2-cyclo-hexanone-carboxylic acids (C. 1910, II. 1378). (6) With PCl_5 unstable dichlorides are first formed, which decompose into HCl and chloro-cyclo-hexenes. (7) $KMnO_4$ and NHO_3 oxidise them clearly to adipinic acids with the grouping $—CO.CH_2—$. (8) By means of Caro's acid some have been split up into lactones (B. **33**, 858). (9) Cyclo-hexanone-oximes are converted into ε-lactames of concentrated H_2SO_4 or PCl_5, and into the nitriles of unsaturated aliphatic acids by P_2O_5 with ring opening (A. **312**, 173; **346**, 266). (10) Sunlight and water partly convert cyclo-hexanones into saturated fatty acids, and the corresponding unsaturated aldehydes (B. **41**, 1071).

	B.p.	D.	
Cyclo-hexanone . . .	155·4°	0·9471 (22°)	
2-Methyl-cyclo-hexanone . .	163°	0·9246 (18°)	C. 1905, I. 742
3-Methyl-cyclo-hexanone . .	168°	0·9111 (18°)	C. 1905, I. 742
4-Methyl-cyclo-hexanone . .	169°	0·9332 (0°)	C. 1905, I. 742
2, 2-Dimethyl-cyclo-hexanone .	170°	0·9141 (20°)	A. **376**, 159
3, 3-Dimethyl-cyclo-hexanone .	174°	..	C. 1907, I. 964
3, 4-Dimethyl-cyclo-hexanone .	187°	..	C. 1906, I. 1248
2, 6-Dimethyl-cyclo-hexanone .	175°	..	B. **27**, 594
2, 4-Dimethyl-cyclo-hexanone .	176·5°	0·9124 (16°)	C. 1906, I. 1248
3, 5-Dimethyl-cyclo-hexanone .	182°	0·8994 (17°)	W. **297**, 163
2, 5-Dimethyl-cyclo-hexanone .	176°	0·9083 (13°)	C. 1906, I. 1248; A. **357**, 202

Cyclo-hexanone-pimelin-ketone, *keto-hexamethylene* $CH_2\langle^{CH_2—CH_2}_{CH_2—CH_2}\rangle CO$ is an oil with an odour like peppermint. It results (1) by the oxidation of cyclo-hexanol; (2) in the reduction of phenol with alternating currents; (3) in the distillation of calcium n-pimelinate or pimelinic anhydride (Vol. I.); (4) by the action of CO_2 upon 1, 5-dibromo-pentane magnesium (C. 1907, II. 681); (5) from nitro-hexamethylene by treatment with glacial acetic acid and zinc dust (A. **302**, 18).

Upon reduction it yields cyclo-hexanol, while nitric acid oxidises it to *adipinic acid* (B. **39**, 2202; C. 1905, I. 1243). By sodium ethylate or HCl two or three molecules of cyclo-hexanone are condensed, with

formation of cyclo-hexylidene-cyclo-hexanone (C_6H_9O) : (C_6H_{10}), **di-cyclo-hexylidene-cyclo-hexanone** (C_6H_{10}) : (C_6H_8O) : (C_6H_{10}), b.p. 214°–217°, and **dodeka-hydro-triphenylene** (B. **40**, 153).

Illumination of an aqueous-alcoholic solution of cyclo-hexanone produces capronic acid and Δ^5-hexene-aldehyde. Cyclo-hexanone-oxime is transposed by concentrated H_2SO_4 in ϵ-capro-lactame (see Vol. I.).

Its *phenyl-hydrazone*, melting at 74°–77°, when acted upon by mineral acids loses ammonia and passes into tetrahydro-carbazol (A. **278**, 100).

With benzaldehyde, cyclo-hexanone condenses to a mono- and a dibenzylidene compound C_6H_5CH : (C_6H_8O), m.p. 53° (B. **40**, 71), and C_6H_5CH : (C_6H_6O) : CHC_6H_5, m.p. 117°. Under special conditions, it was found possible to isolate the intermediately formed mono acid di-aldols, m.p. 102° and 162° (C. 1908, I. 638). With nitrous acid we obtain di-iso-nitro-cyclo-hexanone HON : (C_6H_6O) : NOH, m.p. 200° with decomposition (C. 1909, II. 1549). Chlorine and bromine easily produce substitution, with formation of 1, 2-chloro- and 1, 2-bromo-cyclo-hexanone respectively, b.p.$_{10}$ 82° and b.p.$_{14}$ 89°. With excess of Br a tetrabromide is formed, m.p. 120°, which, on heating, splits off HBr and forms 2, 6-dibromo-phenol (A. **343**, 40 ; *J. pr. Ch.* 2, **80**, 487).

3-Methyl-cyclo-hexanone $CO\langle^{CH_2—CH(CH_3)}_{CH_2———CH_2}\rangle CH_2$ has been obtained in an optically active dextro-form of $[\alpha]_D = +12{\cdot}5°$ by splitting up the natural *pulegone* (B. **30**, 23 ; *J. pr. Ch.* 2, **61**, 477). It is the most accessible hydro-aromatic ketone. On oxidation with HNO_3 we obtain simultaneously α- and β-methyl-adipinic acid (A. **336**, 299). Its oxime, m.p. 44° (A. **332**, 337), is transposed by concentrated H_2SO_4 into a mixture of β- and δ-methyl-ϵ-capro-lactame (A. **346**, 253). On its conversion into m-cresol, see B. **32**, 3338. From 3-methyl-cyclo-hexanone the action of $NaNH_2$ and alkyl iodide produces **1-methyl-4-ethyl-** and **1-methyl-4-propyl-cyclo-hexanone**, b.p.$_{18}$ 84° and 98° respectively, as well as numerous homologous cyclo-hexanones (see synthesis of menthone, below).

2, 2-Dimethyl-cyclo-hexanone is formed from 1-iso-propyl-cyclo-pentane-1, 6-diol by pinacolin transformation and simultaneous ring extension.

3, 5, 5-Trimethyl-cyclo-hexanone, dihydro-iso-aceto-phorone, b.p. 189°, has been obtained from dihydro-iso-aceto-phorol, the reduction product of iso-aceto-phorone, by oxidation with chromic acid mixture. For transposition of the oximes, see A. **346**, 256. **2, 4, 4-Trimethyl-cyclo-hexanone**, b.p. 191°, from 2, 4, 4-trimethyl-cyclo-hexenone (A. **324**, 97). **3, 6, 6-Trimethyl-cyclo-hexanone**, see Pulenone.

Ring-ketols.—**1, 2-Cyclo-hexanolone** $CO\langle^{CH(OH).CH_2}_{CH_2———CH_2}\rangle CH_2$, m.p. 113°, sublimes very easily, and is formed from 1, 2-chloro-cyclo-hexanone with alkalies. It yields on oxidation with $KMnO_4$ adipinic acid (C. 1906, II. 125 ; *J. pr. Ch.* 2, **80**, 488). **Methyl-1, 2-cyclo-hexanolone** $CH_3C_6H_9O(OH)$, b.p.$_{12}$ 86°, from methyl-bromo-cyclo-hexanone (B. **35**, 2695). **3-Methyl-1, 2, 3-cyclo-hexanone-diol** $CH_3C_6H_7O(OH)_2$, m.p. 65°, is formed from the synthetic methyl-cyclo-hexenone and from $\Delta^{1,3}$-dihydro-toluol, by oxidation with $KMnO_4$; on boiling with dilute sulphuric acid it yields methyl-cyclo-hexane-dione (B. **35**, 1176). 1, 3-

Cyclo-hexanolones must be assumed as intermediate products in the formation of cyclo-hexenones from 1, 5-diketones of the formula $C\langle^{C—COCH_3}_{C—COCH_3}$, some of which may be $C\langle^{C—CO—}_{C—C(OH)—}\rangle^{CH_2}_{CH_2}$ (A. **323**, 83; B. **36**, 2118).

Diketo-hexamethylenes, Cyclo-hexane-diones.—Theory indicates three isomeric diketo-hexamethylenes, two of which, the 1, 3- and the 1, 4-diketo-hexamethylene, are known, while of the o-diketo-hexamethylene, up to now only a methyl derivative, **1-methyl-2, 3-diketo-hexamethylene** $CH_3.C_6H_7O_2$, m.p. 65°, has been prepared; it is formed from methyl-cyclo-hexanone-diol by discarding water, and smells strongly of quinone (B. **35**, 1178).

Dihydro-resorcin, 1, 3-*cyclo-hexane-dione, m-diketo-hexamethylene* $CH_2\langle^{CH_2.CO}_{CH_2.CH_2}\rangle CO$ or $CO\langle^{CH=C(OH)}_{CH_2—CH_2}\rangle CH_2$ melts with decomposition at 104°–106°. It is a feeble acid, and probably therefore an unsaturated ketone alcohol of ring formation. It is produced upon introducing pure sodium amalgam into a boiling aqueous resorcin solution while carbon dioxide is being conducted into it. It may be synthesised by the condensation of γ-acetyl-butyric ester with sodium ethylate. Dihydro-resorcin dissolves readily in water, alcohol, and chloroform, but with difficulty in ether. It reacts acid, and decomposes the alkali and alkaline earth carbonates. It can be directly esterified with alcohol and HCl.

It also forms a **dioxime** $C_6H_8(NOH)_2+2H_2O$. This melts at 154°–157° when it is anhydrous; when reduced it becomes m-diamido-hexamethylene. m-Dioxy-hexahydro-iso-phthalo-nitrile (A. **278**, 20) is formed by adding prussic acid to dihydro-resorcin (A. **308**, 184). PCl_3 produces **chloro-keto-tetrahydro-benzol** C_6H_7OCl, b.p.$_{24}$ 104°, whereas PCl_5 produces **dichloro-dihydro-benzol** $C_6H_6Cl_2$, b.p.$_{29}$ 89° (C. 1903, I. 1352); bromine gives **2-bromo-hydro-resorcin** $C_6H_7O_2Br$. NaOBr and bleaching-lime decompose hydro-resorcin into glutaric acid and chloroform (A. **322**, 245); by heating with baryta water to 150°–160° it is broken up into acetyl-butyric acid (A. **294**, 269).

Homologues of dihydro-resorcin are similarly formed in the condensation of like δ-ketone-carboxylic esters, as, for example, in the addition of malonic esters to alkylidene-aceto-acetic ester. When the latter is condensed with malonic ester, through the agency of sodium ethylate, and the product then saponified, carbon dioxide is eliminated, and there results **methyl-dihydro-resorcin**, m.p. 126° (A. **289**, 137; **294**, 253):

$$CO_2RCH.\overset{CH_2}{\overset{|}{C}}H.CHCO_2R \longrightarrow CO_2RCH.\overset{CH_2}{\overset{|}{C}}H.CHCO_2R \longrightarrow CH_2.\overset{CH}{\overset{|}{C}}H.CH_2$$
$$CO.CH_2CO_2R \qquad CO.CH_2.CO \qquad CO.CH_2.CO$$

Iso-propyl-dihydro-resorcin $(CH_3)_2CH.C_6H_7O_2$, m.p. 82° (C. 1902, II. 115). **Phenyl-dihydro-resorcin** $(C_6H_5)C_6H_7O_2$, m.p. 184°. **1, 2-Diphenyl-dihydro-resorcin,** m.p. 160°, from phenyl-acetic ester, benzal-acetone, and sodium ethylate (B. **42**, 4498).

Cinnamenyl-dihydro-resorcin $(C_6H_5CH:CH)C_6H_7O_2$, from cinnamylidene-acetone and Na-malonic ester, is changed, by bleaching-lime, into cinnamenyl-glutaric acid (A. **345**, 206).

Dimethyl-hydro-resorcin $(CH_3)_2C : [CH_2CO] : CH_2$, m.p. 150°, from mesityl oxide, and sodium-malonic ester, gives, with NaOBr and bleaching-lime, $\beta_1\beta$-dimethyl-glutaric acid (A. **368,** 135). For halogen derivatives of dimethyl-hydro-resorcin, see A. **322,** 239. For the transformation of dimethyl-dihydro-resorcin into dimethyl-di- and tetra-hydro-benzol, see C. 1908, I. 1779. **Trimethyl-dihydro-resorcin,** m.p. 100° (C. 1900, I. 1069; 1901, I. 567).

The homologous dihydro-resorcins react like simple dihydro-resorcin, both as diketones and as unsaturated oxy-ketones.

1, 4-Cyclo-hexane-dione, *tetrahydroquinone, p-diketo-hexamethylene* $CO\langle\begin{smallmatrix}CH_2—CH_2\\CH_2—CH_2\end{smallmatrix}\rangle CO$, m.p. 78°, results upon saponifying succino-succinic ester with concentrated sulphuric acid, when it loses carbon dioxide (Baeyer), or when the same body is boiled with aqueous alcoholic hydrochloric acid. On heating succinyl-succinic ester with methyl or ethyl alcohol to 200°, acetals of p-diketo-hexamethylene are formed, methyl acetal, m.p. 81°, ethyl acetal, m.p. 89° (B. **34,** 1344). In small quantities, p-diketo-hexamethylene is also produced by distillation of calcium succinate.

It unites with sodium bisulphite to form a *dioxime*, melting at 192°; the latter is changed by chlorine into **p-dichloro-dinitroso-hexamethylene** $(ON)CCl(CH_2.CH_2)_2CCl(NO)$, deep-blue crystals, m.p. 108°, changed by glacial acetic-hydrochloric acid into a colourless form melting at 128°–130° with decomposition (B. **35,** 3101). With benzaldehyde and HCl p-diketo-hexamethylene forms benzyl-hydroquinone (B. **37,** 3486). It forms *quinite* upon reduction; see also α-Dioxy-hexahydro-terephthalic acid.

p-Dimethyl-p-diketo-hexamethylene, 2, 5-*dimethyl*-1, 4-*cyclo-hexane-dione*, m.p. 93°, is obtained from p-dimethyl-succino-succinic ester (B. **25,** 2122).

Cyclo-hexane-triones.—Phloro-glucin yields derivatives which can be deduced from the formula of 1, 3, 5-trioxy-benzol, and others which can be obtained from the formula of 1, 3, 5-triketo-hexamethylene. It was discussed at the conclusion of pyrogallol and oxy-hydroquinone, as were the hexa-alkyl derivatives of phloro-glucin.

Triquinoyl $C_6O_6+8H_2O$, described with the quinones, is probably *hexaketo-hexamethylene.*

Halogen Substitution Products of the Ring-ketones of Hexahydrobenzol are formed in the continuous action of chlorine and bromine upon phenols, quinones, and oxy-quinones. Several of the keto-chlorides can be readily rearranged into halogen keto-pentene derivatives, and be decomposed into highly chlorinated fatty bodies: ketones, ketonic acids, and fatty acids.

Heptachloro-resorcin, *heptachloro*-1, 3-*cyclo-hexane-dione* $CO\langle\begin{smallmatrix}CCl_2—CO\\CH_2—CHCl\end{smallmatrix}\rangle CH_2$, m.p. 50°, b.p.$_{25}$ 170°, from resorcin and Cl in chloroform (B. **24,** 912).

Quinone tetrabromide, 2, 3, 5, 6-*tetrabromo-cyclo-hexane-dione* $CO\langle\begin{smallmatrix}CHBr.CHBr\\CHBr.CHBr\end{smallmatrix}\rangle CO$. **Hexachloro-triketo-R-hexylene,** *hexachloro*-1, 3, 5-*cyclo-hexane-trione* $CO\langle\begin{smallmatrix}CCl_2—CO\\CCl_2—CO\end{smallmatrix}\rangle CCl_2$, m.p. 48°, b.p. 268°, from phloro-glucin with Cl in chloroform (B. **22,** 1473).

Pentabromo-diketo-oxy-cyclo-hexenol $CO\langle^{CBr_2—C(OH)}_{CBr_2—CO}\rangle CBr + H_2O$, m.p. 119° with decomposition. It is produced when bromine in water acts upon phloro-glucin. It forms amber-yellow-coloured crystals. It is a strong acid.

Hexabromo-triketo-cyclo-hexane $C_6Br_6O_3$ melts at 147° (B. **23**, 1729).

Tri- and **tetrachloro-tetraketo-cyclo-hexanes** $CO\langle^{CO—CCl_2}_{CCl_2—CO}\rangle CO$. They are obtained from chloranilic acid and chlorine. The corresponding bromine derivatives are made from bromanilic acid (B. **25**, 845).

(*b*) *Ring-ketones from the Tetrahydro-benzenes* can be synthesised by condensing aceto-acetic ester, acetone-dicarboxylic ester, and analogous compounds with aldehyde iodides, like methylene iodide, or with aldehydes in the presence of small quantities of bases, such as diethylamine or piperidin, to 1, 5-diketone-carboxylic esters—*e.g.* methylene-, ethylidene-, iso-butylidene-diaceto-acetic ester and methylene bis-acetone-dicarboxylic ester. When the latter are treated with hydrochloric acid in ether, they first form a ring and become carboxylic esters of Δ_2-keto-R-hexenes, and then, when acted upon with alkalies or dilute acids, are saponified, split off CO_2, and change to the ketones themselves (A. **289**, 131) :

$$\begin{array}{l} CO_2.C_2H_5.CH.CO.CH_3 \\ \quad\quad\quad | \\ \quad\quad\quad CH_2 \\ \quad\quad\quad | \\ CO_2.C_2H_5.CH.CO.CH_3 \end{array} \xrightarrow{-H_2O} \begin{array}{l} CO_2.C_2H_5.CH.C.CH_3 \\ \quad\quad\quad | \quad\quad || \\ \quad\quad\quad CH_2CH \\ \quad\quad\quad | \quad\quad | \\ CO_2.C_2H_5.CH.CO \end{array} \longrightarrow \begin{array}{l} CH_2.C.CH_3 \\ \quad\quad | \quad\quad || \\ CH_2\ CH \\ \quad\quad | \quad\quad | \\ CH_2.CO \end{array}$$

From acetyl-acetone with aldehydes we obtain δ_2-tetraketone $(CH_3COCH)_2CHR(CHCOCH_3)_2$, which, on twofold ring condensation, yields dicyclic systems whose structure has still to be determined (B. **30**, 2136).

From the nitroso-chlorides of some cyclo-hexenes Δ^2-cyclo-hexenones have been prepared by splitting off HCl by means of sodium ethylate or sodium acetate and glacial acetic acid, and breaking up the resulting oximes with oxalic acid or phthalic anhydrides.

By reduction with sodium and alcohol we obtain from Δ^2-cyclo-hexenones the saturated cyclo-hexanols. But if we reduce with sodium amalgam in acid solution, two molecules are combined and we obtain derivatives of *diketo-perhydro-diphenyl*. **3-Methyl-Δ^2-cyclo-hexenone** $CH_2\langle^{CH_2—CH_2}_{CO\quad CH_2}\rangle C(CH_3).C(CH_3)\langle^{CH_2—CH_2}_{CH_2\quad CO}\rangle CH_2$. By the action of two molecules of hydroxylamine, oximes are formed. Thus, from 3-methyl-Δ^2-cyclo-hexenone we get 3-methyl-3-hydroxylamino-cyclo-hexanone-oxime (B. **32**, 1315).

Δ^2-Cyclo-hexenone $CO\langle^{CH=CH}_{CH_2—CH_2}\rangle CH_2$, b.p.$_{14}$ 63°, bromo-cyclo-hexanone, on boiling with aniline, or from 1, 2-cyclo-hexanolone with anhydrous oxalic acid. Its unstable dibromide easily passes into phenol by splitting off HBr. The oxime melts at 75° and yields aniline on boiling with acetic anhydride. Oxamine oxime, m.p. 50° (*J. pr. Ch.* 2, **80**, 487).

3-Methyl-Δ^2-cyclo-hexenone $CO\langle^{CH=C(CH_3)}_{CH_2—CH_2}\rangle CH_2$, b.p. 200°, forms

a mobile liquid of pleasant odour. Its bromine addition-product decomposes spontaneously into BrH and m-cresol. It seems to exist in two isomeric forms, one of which can be mixed with water, while the other is difficult to dissolve. They are of identical chemical behaviour, and both are oxidised by permanganate to γ-acetyl-butyric acid (B. **40,** 2482). The oxime, m.p. 89°, gives, on boiling with acetic anhydride, m-toluidin (A. **322,** 382). The hydroxylamino-oxime, m.p. 84°, gives, by oxidation with mercuric oxide, a nitroso-oxime. By heating with concentrated potash, the 3-methyl-Δ^2-cyclo-hexenone is changed into a polymerisation product resembling an aldol, melting at 113° (B. **32,** 423; A. **297,** 142). With sodium-aceto-acetic ester it combines to form 5-diketone-carboxylic ester, which by ring-condensation passes into a *bicyclic* ketone-alcohol (B. **37,** 1671).

2-Methyl-Δ^2-cyclo-hexenone $CO\langle\begin{matrix}C(CH_3)=CH\\CH_2---CH_2\end{matrix}\rangle CH_2$, b.p. 179°, from the nitroso-chloride of Δ^1-methyl-cyclo-hexene (A. **359,** 303).

4-Iso-propyl-Δ^2-cyclo-hexenone $CO\langle\begin{matrix}CH=CH\\CH_2—CH_2\end{matrix}\rangle CH.C_3H_7$, b.p.$_{12}$ 94°, semi-carbazone, m.p. 185°, is formed by heating sabina-ketone and nopinone with dilute sulphuric acid and by the self-oxidation of β-phellandrene. It polymerises very easily, especially in the presence of alkali. With methyl-magnesium iodide water is split off and α-phellandrene is formed (A. **359,** 270).

4-Iso-propyl-Δ^3-cyclo-hexenone $CO\langle\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}\rangle C.C_3H_7$, b.p.$_{12}$ 95°, semi-carbazone, m.p. 170°, is formed from the HCl addition product of sabina-ketone by heating with dimethyl-aniline. Mineral acids transpose it into the Δ^2-ketone. With methyl-magnesium iodide it yields terpinenol-1 (A. **362,** 280).

1, 4-Iso-propylidene-cylo-hexanone $CO\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle C:C\langle\begin{matrix}CH_3\\CH_3\end{matrix}$, b.p. 220°, semi-carbazone, m.p. 200°, from the corresponding carboxylic ester (C. 1907, II. 1975). **1, 4-Iso-propenyl-cyclo-hexanone** $CO\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle CH.C\langle\begin{matrix}CH_3\\CH_3\end{matrix}$, b.p.$_{300}$ 185° (C. 1904, II. 331).

3, 5-Dimethyl-Δ^2-cyclo-hexenone, b.p. 211°. Its dibromide easily passes into sym. xylenol (A. **281,** 121); its oxime, m.p. 68°-74°, is transposed, by heating with HCl, into sym. xylidene (A. **322,** 381).

5, 5-Dimethyl-Δ^2-cyclo-hexenone, b.p.$_{32}$ 85·5°, from dimethyl-chloro-cyclo-hexanone, the product of the action of PCl_3 upon dimethyl-dihydro-resorcin, by reduction with zinc dust. With permanganate it gives α-oxy-$\beta_1\beta$-dimethyl-glutaric acid and unsym. dimethyl-succinic acid (C. 1907, I. 1039).

3, 5, 5-Trimethyl-Δ^2-cyclo-hexenone, iso-aceto-phorone, *iso-phorone* $C_9H_{14}O=CO\langle\begin{matrix}CH=C(CH_3)\\CH_2—C(CH_3)_2\end{matrix}\rangle CH_2$, boiling at 89° (10 mm.), is produced in the condensation of mesityl oxide with aceto-acetic ester, saponification, and elimination of carbon dioxide from the carboxylic ester formed at first. It also results from the condensation of acetone by means of lime or sodium ethylate. It is isomeric with phorone, camphor-phorone, iso-camphorone, nopinone, camphenilone, and fencho-camphorone. Upon reduction with sodium and alcohol it forms *dihydro-iso-phorol* $C_9H_{17}(OH)$, which by loss of water becomes

trimethyl-cyclo-hexene, and by the reduction of its iodide yields *trimethyl-cyclo-hexane*. When oxidised with potassium permanganate the ring is ruptured and various acids result: $\gamma\gamma$-dimethyl-α, 2-diketo-heptylic acid $C_9H_{14}O_4$, γ-acetyl-$\beta\beta$-dimethyl-butyric acid $C_8H_{14}O_3$, and unsym. dimethyl-succinic acid (C. 1909, I. 853).

The iso-phorone gives two isomeric oximes melting at 75° and 100° respectively (A. **297,** 187; **299,** 165, 193), which are transposed, by heating with HCl to 170°, into 1-amido-3, 4, 5-trimethyl-benzol (A. **322,** 379). Besides iso-phorone, we find among the condensation products of acetone more highly condensed ketones, the so-called *xylitones* $C_{12}H_{18}O$, probably formed by condensation of a further molecule of acetone with iso-phorone; the xylitones produced by different condensation agents, such as lime, sodium ethylate, and HCl, seem all to differ from one another. An identically situated xylitone, which, however, is not identical with any of the others, and melts at 133° (12 mm.), has been obtained by the addition of sodium-aceto-acetic ester and phorone. By boiling with formic acid it is split up into acetone and iso-phorone (B. **39,** 3441).

2, 4, 4-Trimethyl-Δ^2-cyclo-hexenone, b.p. 196°, by transformation of α-cyclo-geraniolene nitroso-chloride (A. **324,** 97).

3-Methyl-5-iso-propyl-Δ^2-cyclo-hexenone $CO\langle\begin{matrix}CH=\!=\!=C(CH_3)\\CH_2-CH(C_3H_7)\end{matrix}\rangle CH$ boils at 244°. Its dibromide passes readily into sym. carvacrol (B. **26,** 1089; **27,** 2347; A. **288,** 357).

3-Methyl-5-iso-butyl- and **3-methyl-5-hexyl-Δ^2-cyclo-hexenones** boil at 147° and at 167° (22 mm.) (B. **288,** 336, 344).

Those chemists who consider the quinones to be ketones regard *rhodizonic acid* as a tetraketo-tetrahydro-benzol derivative.

4-Methyl- and **2, 4-dimethyl-Δ^2-cyclo-hexenones,** b.p. 192° and 194°, are found among the ketones of wood-tar (C. 1901, I. 611).

Halogen Substitution Products of Ring-ketones of Tetrahydro-benzols result when chlorine acts upon phenols, anilines, oxy-benzoic acids, etc. They can be very readily broken up.

Heptachloro-keto-tetrahydro-benzols $CCl_2\langle\begin{matrix}CCl=\!=CCl\\CHCl-CCl_2\end{matrix}\rangle CO$ and $CCl\langle\!\!\langle\begin{matrix}CCl-\!-CCl_2\\CHCl-CCl_2\end{matrix}\rangle CO$, the α-body melting at 98° and the β-modification at 80°, result from the action of chlorine upon m-chloraniline (B. **27,** 547).

Octo-chloro-keto-tetrahydro-benzol $CCl_2\langle\begin{matrix}CCl=\!=CCl\\CCl_2-CCl_2\end{matrix}\rangle CO$, or $CCl\langle\!\!\langle\begin{matrix}CCl-\!-CCl_2\\CCl_2-CCl_2\end{matrix}\rangle CO$, melting at 103°, result from the action of chlorine upon pentachloro-phenol in glacial acetic acid, and from perchloro-m-oxy-benzoic acid. Reducing agents change it into pentachloro-phenol (B. **27,** 550).

Hexachloro-o-diketo-tetrahydro-benzol $CCl_2\langle\begin{matrix}CCl_2-CO\\CCl=\!=CCl\end{matrix}\rangle CO + 2H_2O$ melts at 93° with decomposition. It is formed when chlorine acts upon pyro-catechol and o-amido-phenol chlorohydrate dissolved in acetic acid. Stannous chloride reduces it to cyclo-benzo-quinone. Homologous o-diketo-chlorides have been obtained from o-diamido-methyl-benzols (B. **27,** 560).

Pentachloro-m-diketo-tetrahydro-benzol $CO\langle\begin{matrix}CCl_2—CO\\CCl=CH\end{matrix}\rangle CCl_2$, m.p. 92° and b.p. 160° (25 mm.), results when chlorine acts upon resorcin in chloroform (B. **28,** 3777).

Hexachloro-m-diketo-tetrahydro-benzol $CO\langle\begin{matrix}CO—CCl_2\\CCl=CCl\end{matrix}\rangle CCl_2$, m.p. 115° and b.p. 159° (14 mm.), is produced when chlorine acts upon 3, 5-dioxy-benzoic acid dissolved in glacial acetic acid (B. **25,** 2688).

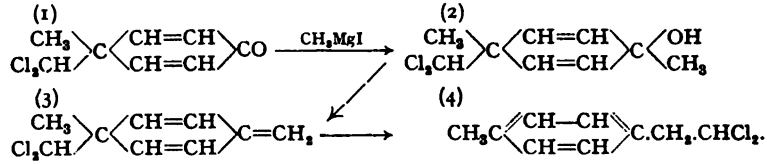
Hexachloro-p-diketo-tetrahydro-benzol $CO\langle\begin{matrix}CCl_2—CCl_2\\CCl=CCl\end{matrix}\rangle CO$, m.p. 89° and b.p. 184° (45 mm.), is formed when chlorine acts upon p-amido-phenol hydrochloride in glacial acetic acid (A. **267,** 16).

(*c*) *Ring-ketones of the Dihydro-benzols.*—There are two possible dihydro-benzols, and from each one monoketone can be obtained. Both bodies are not yet known, but in **tetrachloro-keto-dihydro-benzol** $Cl\langle\begin{matrix}CH—CCl_2\\CH=CCl\end{matrix}\rangle CO$, or $CCl_2\langle\begin{matrix}CH=CCl\\CH=CCl\end{matrix}\rangle CO$, m.p. 106°, we have chlorine derivatives of one or of both keto-dihydro-benzols. The first body is formed from trichloro-phenol and chlorine, and the second, most conveniently, by heating (B. **27,** 546) the heptachloro-keto-tetrahydro-benzol, melting at 98°, and by treating phenol, anisol, and pentachloraniline with chlorine (B. **28,** R. 63).

Among the ring-ketones of the dihydro-benzols we must also include a series of substances obtained as by-products in the action of chloroform and alkali, or of carbon tetrachloride and aluminium chloride upon o- and p-alkylated phenols, *e.g.* :

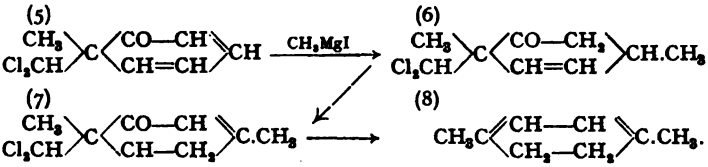
$$CO\langle\begin{matrix}CH=CH\\CH=CH\end{matrix}\rangle C\langle\begin{matrix}R\\CHCl_2\end{matrix}, \quad CO\langle\begin{matrix}CH=CH\\CH=CH\end{matrix}\rangle C\langle\begin{matrix}R\\CCl_3\end{matrix}, \quad CH\langle\begin{matrix}CH—CO\\CH=CH\end{matrix}\rangle C\langle\begin{matrix}R\\CHCl_2\end{matrix}$$

Thus, compounds which are reconverted into the original phenols by reduction with zinc dust and glacial acetic acid, and reduction of CH_2Cl_2 or $CHCl_3$, react with phenyl-hydrazin, hydroxylamine, and semi-carbozide like ketones (B. **36,** 1861). Special interest attaches to the further transformations of these ketones with alkyl-magnesium compounds. The ketones (1) derived from the p-alkyl-phenols yield normal tertiary alcohols (2) which easily split off water and become unstable alkylidene-dihydro-benzols (3), and change into true benzol derivatives (4) on heating at ordinary temperatures with migration of the $CHCl_2$ group or the CCl_3 group (A. **352,** 219).



Different behaviour is shown by the ketones derived from the o-alkyl-phenols. These (5) attach the alkyl-magnesium compounds to the carbon double link and form higher homologous β, γ-unsaturated ketones (6), which, by the action of concentrated sulphuric acid, displace the double link and pass into the isomeric α, β-unsaturated ketones (7). The latter, on heating with alcoholic potash, yield

1, 4-dialkyl-cyclo-hexadienes (8), by a curious reaction with intermediate formation of p-dialkyl-dihydro-benzoic acids (B. **42**, 2404):



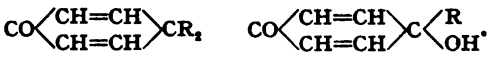
By using iso-propyl-magnesium iodide we get a synthesis of *α*-terpinene (Auwers).

1-Methyl-4-dichloro-methyl-keto-dihydro-benzol, m.p. 55°, changes, under the action of PCl_5, with intermediate formation of an unstable tetrachloride and migration of the methyl group, into trichloro-o-xylol $Cl[5]C_6H_3[1]CH_3[2]CHCl_2$. With CH_3MgI it forms **1, 4-dimethyl-4-dichloro-methyl-oxy-dihydro-benzol** (2), m.p. 96°, which easily decomposes into water and **1-methylene-4-methyl-4-dichloro-methyl-dihydro-benzol** (3), a yellowish oil. On heating, the latter transposes into **1-methyl-4-(*β*)-dichlorethyl-benzol** (4), which, with concentrated H_2SO_4, passes into m-xylol-aldehyde, with migration of the methyl group.

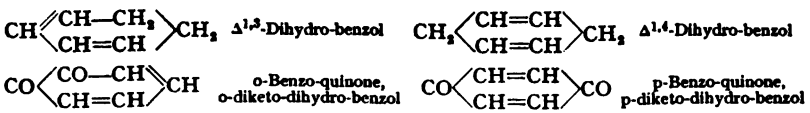
4-Methyl-4-trichloro-methyl-keto-dihydro-benzol $CH_3C(CCl_3)\langle CH{=}CH \rangle CO$, m.p. 105°, oxime, m.p. 134°, from p-cresol, CCl_4, and $AlCl_3$, behaves like the corresponding dichloro-compound (B. **41**, 897).

2-Methyl-2-dichloro-methyl-keto-dihydro-benzol (5), m.p. 33°, b.p.$_9$ 113°, gives, with CH_3MgI, **3, 6-dimethyl-6-dichloro-methyl-Δ^4-cyclo-hexenone,** *dichloro-β, γ-pulenone* (6), b.p. 124° (15 mm.), which is converted by H_2SO_4 into the isomeric **3, 6-dimethyl-6-dichloro-methyl-Δ^3 cyclo-hexenone,** *dichloro-αβ-pulenone* (7), m.p. 41°, b.p.$_{15}$ 151°; the latter, with alcoholic potash, gives **$\Delta^{1,3}$-dihydro-p-xylol** (8), and by reduction with Na and alcohol **3, 6, 6-trimethyl-cyclo-hexanol** or pulenol.

The *methylene-quinones* and *quinols*, discussed in connection with phenol alcohols, are probably also monoketones, derivable from $\Delta^{1,4}$-dihydro-benzol:



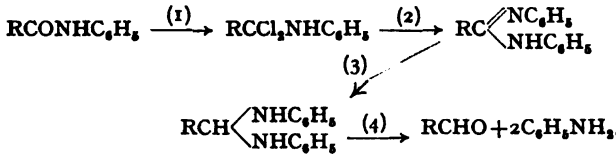
Each of the possible dihydro-benzols also yields a diketone:



If the diketone formula is preferred for the benzo-quinones, previously discussed with the phenols, then p-benzo-quinone is p-diketo-dihydro-benzol, and its numerous derivatives are also deducible from the latter compound. o-Benzo-quinone would be o-diketo-dihydro-benzol.

(5) Hydro-aromatic Aldehydes.

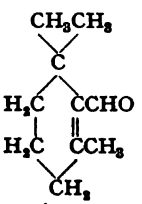
Concerning the production of hydro-aromatic aldehydes, which is connected in general with well-known reactions, we must remark that their production from the calcium salts of the hydro-aromatic carboxylic acids, by distillation with calcium formate, is not a straightforward reaction, and is often accompanied by transpositions. On the other hand, the conversion of the hydro-aromatic carboxylic acids into the corresponding aldehydes, by the transformation of the acid anilides into the anilide chlorides (1), and diphenyl-amidines (2), the reduction of the latter with sodium and alcohol (3), and the splitting up of the resulting alkylidene-dianilines with dilute sulphuric acid (4), can be successfully carried out (B. **41**, 2064).



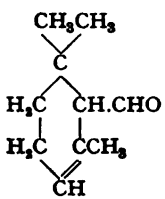
Hexahydro-benzaldehyde $C_6H_{11}.CHO$, b.p. 162°, is formed (1) by oxidising cyclo-hexyl-carbinol with chromic acid; (2) from the glycol of methene-cyclo-hexane with dilute H_2SO_4 (A. **347**, 331); (3) from the synthetic cyclo-hexyl-glycidic ester by saponification and CO_2 rejection (C. 1906, I. 1423). It smells of oil of bitter almonds and valeraldehyde, and polymerises readily to **meta-hexahydro-benzaldehyde** $(C_7H_{12}O)_2$, m.p. 202° (B. **40**, 3050). **Oxime,** m.p. 91°; **semicarbazone,** m.p. 174°. By methods 2 and 3 numerous homologous aldehydes have been obtained: **o-, m-,** and **p-hexahydro-tolyl-aldehydes** $CH_3.C_6H_{10}CHO$, b.p.$_{15}$ 61°, 60°, and 63°. **2, 6, 6-Trimethyl-hexahydro-benzaldehyde,** b.p.$_{10}$ 59°, by reduction of β-cyclo-citral with H and colloidal palladium (B. **42**, 1635).

Δ^1-Tetrahydro-benzaldehyde $C_6H_9.CHO$, an oil smelling strongly of benzaldehyde, formed by HCl rejection from the nitroso-chloride of methene-cyclo-hexane, by means of sodium acetate and glacial acetic acid. **Oxime,** m.p. 58°. **Semi-carbazone,** m.p. 212°. In a similar manner the *tetrahydro-tolyl-aldehydes* are formed (A. **359**, 292). **Δ^3-Tetrahydro-benzaldehyde,** b.p.$_{17}$ 58°, from Δ^3-bromo-cyclo-hexene-magnesium and orthoformic ester (B. **43**, 1040).

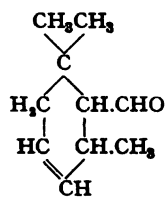
2, 6, 6-Trimethyl-tetrahydro-2-benzaldehydes, cyclo-citrals.—Of these aldehydes, important for the synthesis of violet perfumes, all four linkage isomers are known:



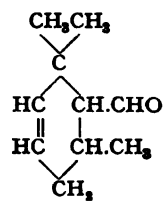
Δ^1- or **β-cyclo-citral**



Δ^2- or **α-cyclo-citral**



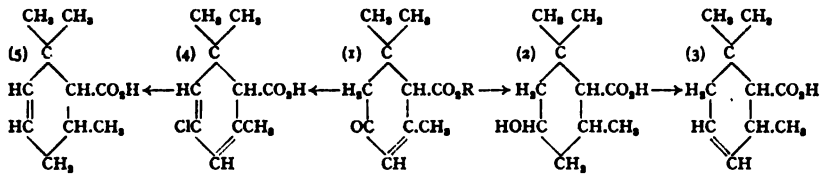
Δ^3-cyclo-citral



Δ^4-cyclo-citral.

α-Cyclo-citral, b.p.$_{20}$ 90°–95°, D 0·925, semi-carbazone, m.p. 204°, and **β-cyclo-citral,** b.p.$_{10}$ 88°–91°, D$_{20}$ 0·957, semi-carbazone, m.p. 167°, are obtained together from the α-cyclic terpene-alcohol citral by changing the latter into aniline, and then condensing to a ring by means of sulphuric and phosphoric acids (C. 1901, II. 716). See also B. **38,** 3720. They are also produced by the oxidation of cyclo-geraniol. α- and β-Cyclo-citral oxidise in air to the corresponding cyclo-geranic acids. With acetone and sodium alcoholate α-cyclo-citral condenses to α-ionone, and β-cyclo-citral to β-ionone.

For the synthesis of Δ^3- and Δ^4-cyclo-citrals we start from iso-phorone-carboxylic ester (1), which, by reduction with Na, yields a mixture of cis-trans-isomeric oxy-acids (2), which, on discarding water, pass into Δ^3-cyclo-geranium acids (3). PCl_5 changes the iso-phorone-carboxylic ester into δ-chloro-cyclo-geraniol-adiene-carboxylic acid (4), from which, by reduction, together with the Δ^2- and Δ^3-acids, Δ^4-cyclo-geranium acid (5) is obtained :



The Δ^3- and Δ^4-cyclo-geranium acids so obtained are changed by the method given above into **Δ^3-cyclo-citral,** b.p.$_{12}$ 76°, and **Δ^4-cyclo-citral.** With acetone the Δ^3-cyclo-citral condenses to **α-irone,** and the Δ^4-cyclo-citral to **β-irone,** which is identical with the irone extracted from violet roots (Merling and Welde, A. **366,** 119). Isomeric trimethyl-tetrahydro-benzaldehydes, see C. 1903, II. 78.

Dihydro-benzaldehyde $C_6H_7.CHO$, b.p.$_{120}$ 122°, is formed from anhydro-ecgonin dibromide (*q.v.*) with sodium carbonate. By gentle oxidation with Ag_2O it gives $\Delta^{1,3}$-dihydro-benzoic acid (B. **26,** 454 ; **31,** 1545).

Dihydro-cumin-aldehyde $C_3H_7.C_6H_6.CHO$, semi-carbazone, m.p. 202° ; oxime, m.p. 43° ; by reduction of nitro-β-phellandrene (A. **340,** 3).

(6) Extra-cyclic Hydro-aromatic Ketones.

Among these compounds we have the important violet perfumes, irone and the ionones.

Preparation.—(1) Oxidation of extra-cyclic secondary alcohols ; (2) from α-alkyl-cyclo-hexyl-glycidic esters by saponification and rejection of CO_2 ; (3) by condensation of cyclo-hexanone with acetic ester and sodium ; (4) ring-unsaturated ketones are obtained from the nitroso-chlorides of alkylidene-cyclo-hexanes by deprivation of HCl and splitting up the resulting oximes (A. **360,** 39).

Hexahydro-aceto-phenone $C_6H_{11}.COCH_3$, b.p.$_{12}$ 68°, by methods 1 and 2, and from the synthetic α-acetyl-cyclo-hexane-carboxylic ester. **2-, 3-** and **4-Methyl-hexahydro-aceto-phenone** $CH_3.C_6H_{10}.COCH_3$, b.p.$_{18}$ 78°, b.p.$_{38}$ 99°, and b.p.$_{14}$ 75°, by method 2 (C. 1907, II. 332).

1, 1-Methyl-acetyl-cyclo-hexane $CH_2\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle C\langle\begin{matrix}COCH_3\\CH_3\end{matrix}$, b.p.$_{18}$

83°, from iso-propyl-cyclo-hexane-1, 7-diol with dilute SO_4H_2 (C. 1910, II. 466).

Hexahydro-propio-phenone $C_6H_{11}.CO.CH_2.CH_3$, b.p. 196°, by oxidation of cyclo-hexyl-ethyl-carbinol, or by action of zinc ethyl upon hexahydro-benzoyl-chloride (B. **42**, 2230).

Cyclo-hexyl-acetone $C_6H_{11}.CH_2.CO.CH_3$, b.p. 196°, from cyclo-hexyl-aceto-acetic ester (B. **42**, 2236).

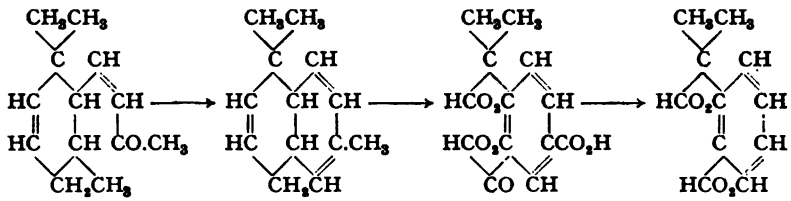
2-Acetyl-cyclo-hexanone $C_6H_9O.COCH_3$, b.p.$_{18}$ 111°, by method 3. Alkalies break it up into acetyl-capronic acid. It can be alkylated by means of sodium and alkyl iodide (C. 1906, I. 252).

3, 6-Methyl-acetyl-cyclo-hexanone $C_6H_8O[3, 6](CH_3)(COCH_3)$, b.p.$_{14}$ 122° (C. 1901, I. 683). **2-Propionyl-cyclo-hexanone** $C_6H_9O.COC_2H_5$, b.p.$_{21}$ 123°, is formed by nuclear synthesis from z-ketononylic ester and Na ethylate (C. 1909, II. 119).

Δ^1-Tetrahydro-aceto-phenone $CH_2\langle\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}\rangle C.COCH_3$, b.p. 201°, from the nitroso-chloride of ethylidene-cyclo-hexane, and by the action of acetyl chloride and $AlCl_3$ upon cyclo-hexene. Oxime, m.p. 99° (C. 1910, I. 1785).

4-Methyl-Δ^1-tetrahydro-aceto-phenone, b.p. 213°. An isomeric **4-methyl-Δ^3-tetrahydro-aceto-phenone,** b.p. 206°, has been obtained by the oxidation of β-terpineol (A. **324**, 89).

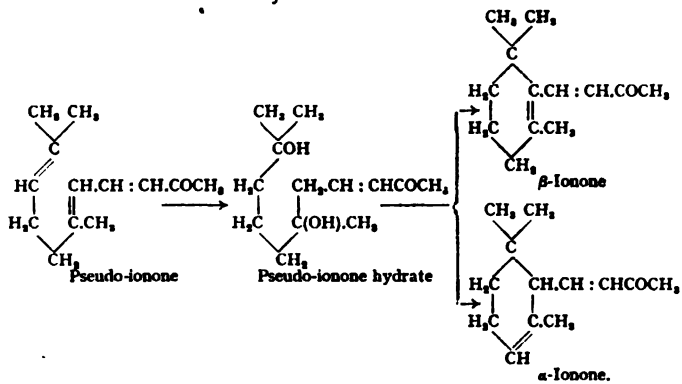
Irone (formula below), b.p. 144°, D_{20} 0·939, $[\alpha]_D = +44°$, was obtained by Tiemann and Krüger (B. **26**, 2675) from the etheric oil of so-called violet root of *Iris florentina, Iris germanica,* and *Iris pallida.* When diluted, it possesses an intense smell of violets. On boiling with HI and P, irone splits off water and forms *irene,* a hydrated naphthalene hydrocarbon, which can be broken up by a series of oxidations into dehydro-irene, iregenone-di- and tri-carboxylic acid, ion-iregene-tricarboxylic acid, and dimethyl-homo-phthalic acid :



α-Ionone, b.p.$_{12}$ 127°, D_{20} 0·9301, and **β-Ionone**, b.p.$_{10}$ 127°, D_{20} 0·9442 (Tiemann, B. **26**, 2691 ; **31**, 808), possess an intense odour of violets closely approaching that of irone, and they are therefore made on a large scale. Their occurrence in the vegetable kingdom has not yet been established with certainty. They are formed by condensation of α- and β-cyclo-citral with acetone and sodium ethylate, or by inversion of pseudo-ionone by means of concentrated sulphuric acid, phosphoric acid, or by heating with aqueous salt solutions to 190° under pressure (C. 1905, I. 783).

In the latter case we obtain a mixture of various quantities of

α- and β-ionone, the formation of which can be explained by the successive attachment and rejection of water :



The pseudo-ionone hydrate, assumed as an intermediate product, has been isolated (C. 1906, II. 723). The constitution of the two ionones follows from their decomposition products : α-ionone gives, on oxidation, ββ-dimethyl-adipinic acid ; β-ionone gives αα-dimethyl-adipinic acid.

(7) Hydro-aromatic Carboxylic Acids.

Attached to the hydro-aromatic hydrocarbons, alcohols, amines, aldehydes, and ketones are numerous hydro-aromatic carboxylic acids. In addition to the simple carboxylic acids, oxy- and keto-carboxylic acids are also known. *Shikimic* and *quinic acids* belong to the first class, while in the second class we find succino-succinic ester and other important ketone-carboxylic esters, which are of great value in the synthesis of the simple hydro-aromatic derivatives.

1. Hydro-aromatic Monocarboxylic Acids.

A direct introduction of the carboxyl group into the nucleus of hydro-aromatic substances can be brought about by the action of CO_2 upon the cyclo-hexyl-magnesium haloids :

$$C_6H_{11}I \xrightarrow[CO_2]{Mg} C_6H_{11}CO_2MgI \xrightarrow{HCl} C_6H_{11}CO_2H.$$

But the transposition of halogen-cyclo-hexanes with KCN or Na malonic ester either does not succeed at all, or is uneconomic, since cyclo-hexenes are mostly formed and H haloids split off :

1-Methyl-cyclo-hexane-1-carboxylic acid	m.p. 39°,	b.p. 234°	(B. **40**, 2069)
trans-Hexahydro-o-toluylic acid . .	m.p. 51°,	b.p. 241°	(B. **41**, 2679)
cis-Hexahydro-o-toluylic acid . .	liquid,	b.p. 236°	(B. **41**, 2679)
Hexahydro-m-toluylic acid .. .	liquid,	b.p. 240°	
α-Hexahydro-p-toluylic acid . .	m.p. 110°,	b.p. 246°	
β-Hexahydro-p-toluylic acid . .	liquid		
2, 4-Hexahydroxylylic acid . .	m.p. 77°,	$b.p._{40}$ 156°	
3, 4-Hexahydroxylylic acid . .	liquid,	b.p. 251°	
2, 6-Hexahydroxylylic acid . .	m.p. 72°,	b.p. 251°	
3, 5-Hexahydroxylylic acid . .	liquid,	b.p. 139°	
Hexahydro-cuminic acid . .	m.p. 96°.		

Hexahydro-benzoic Acids, hexamethylene-carboxylic acids, *naphthenic acids*, have been obtained by the reduction of boiling amyl or capryl solutions of benzoic acid and its homologues with metallic sodium, or by reducing the solution of sodium benzoate with sodium in an atmosphere of CO_2 (B. **24,** 1865; **25,** 3355). So far as present experience warrants, they are isomeric and not identical (B. **27,** R. 195, 197) with the " natural naphthenic acids " occurring in the oil which issues from the earth in and about Baku. Just as fatty acids have been prepared from malonic acids, so hexamethylene-monocarboxylic acids have been obtained by heating hexamethylene-1, 1-dicarboxylic acids. The latter bodies have been prepared synthetically.

The hexamethylene-carboxylic acids are weak acids. They are reduced, when heated with hydriodic acid, to hexahydro-aromatic hydrocarbons—*naphthenes*, containing a like number of C-atoms in the molecule. Hence they are also designated as *naphthenic acids*.

Hexahydro-benzoic acid, *naphthenic acid* $C_6H_{11}.CO_2H$, melting at 28° and boiling at 232°, results from the reduction of benzoic acid, Δ^2-tetrahydro-benzoic acid (A. **271,** 261), p-dimethyl-amido-benzoic acid (B. **27,** 2829), and cyclo-hexanol-1-carboxylic acid (B. **27,** 1231); also by heating hexamethylene-1, 1-dicarboxylic acid, and from chloro-, bromo-, and iodo-cyclo-hexane with Mg and CO_2 (B. **35,** 2688). The *calcium salt* $(C_7H_{11}O_2)_2Ca+5H_2O$. The *methyl ester* boils at 182°. The *ethyl ester* boils at 194°, and the *amide* melts at 185°. The chloride boils at 179° (B. **30,** 1941).

The acids are prepared partly by the reduction of the corresponding benzol-carboxylic acids, and partly by the action of Mg and CO_2 upon the halogen-cyclo-hexanes. Hexahydro-o-toluic acid is formed from 2-methyl-cyclo-hexane-1, 1-acetyl-carboxylic ester and 1, 1-dicarboxylic ester. The liquid cis-acid has been obtained by reduction of its bromine substitution product. The liquid p-hexahydro-toluic acid has been obtained from tropilidene-carboxylic acid (*J. pr. Ch.* 2, **57,** 102; B. **32,** 1167; C. 1899, II. 387).

α-Monobromo-hexahydro-benzoic acid, melting at 63°, and **α-Monobromo-hexahydro-p-toluic acid,** melting at 71°, are produced by acting with bromine upon the chlorides of the corresponding hexahydro-acids. From hexahydro-m-toluic acid two isomeric monobromo-derivatives are obtained, melting at 118° and 142° respectively (B. **32,** 1167).

α-Amido-hexahydro-benzoic acids have been obtained by action of ammonium cyanide upon cyclo-hexanones and saponification of the resulting α-amido-acid nitriles (B. **41,** 2925).

α-Amido-hexahydro-benzoic acid $C_5H_{10}>C(NH_2)COOH$, m.p. 335°.

Hexahydro-anthranilic acid, *o-amido-hexahydro-benzoic acid* $NH_2[2]C_6H_{10}.CO_2H$ melts with decomposition at 274°. It is formed along with pimelic and hexahydro-benzoic acids in the reduction of anthranilic acid with Na and amyl-alcohol (B. **27,** 2470; A. **295,** 187). **Hexahydro-m-amido-benzoic acid,** m.p. 269°, ethyl ester, b.p.$_{11}$ 123°, from m-amido-benzoic acid by reduction with Na and ethyl- or amyl-alcohol, together with other bodies (A. **319,** 324). **Hexahydro-p-dimethyl-amido-benzoic acid** (B. **27,** 2831).

Derivatives of o-amido-hexahydro-phenyl-acetic acid and propionic acid result on oxidising dekahydro-quinolin compounds with potassium permanganate.

Octohydro-carbostyril $C_6H_{10}\begin{cases}CH_2.CH_2\\ \quad|\\ NH.CO\end{cases}$ melting at 151°, is poisonous (B. **27**, 1472). Numerous further amido-cyclo-hexane-carboxylic acids have been obtained from the oximes of the cyclo-hexanone- and cyclo-hexenone-carboxylic ester by reduction with Na and alcohol (B. **40**, 4167).

trans-Diethyl-hexahydro-benzyl-amine-o-carboxylic acid $(C_2H_5)_2N\,CH_2[2]C_6H_{10}COOH$, m.p. 101°, from o-diethyl-benzyl-amine-carboxylic acid, by reduction with sodium and amyl-alcohol. By heating with alkalies it is transposed into the more strongly basic, betaïn-like, oily cis-acid, which is easily decomposed into diethyl-amine and **o-methylol-hexahydro-benzoic acid** $HOCH_2.C_6H_{10}COOH$, m.p. 112°. This latter acid, on heating, gives hexahydro-phthalide $C_6H_{10}\langle\begin{matrix}CH_2\\ CO\end{matrix}\rangle O$ (A. **300**, 161).

For **hexahydro-p-benzyl-amine-** and **p-diethyl-benzyl-amine-carboxylic acids,** see A. **310**, 189.

Tetrahydro-benzoic Acids can be obtained from the monoxy- and monobromo-cyclo-hexane-carboxylic acids by splitting off H_2O or HBr, and also by the reduction of the benzoic acids and dihydro-benzoic acids (B. **26**, 457).

Δ^1-Tetrahydro-benzoic acid $CH_2\langle\begin{matrix}CH_2.CH_2\\ CH_2.CH_2\end{matrix}\rangle C.CO_2H$, m.p. 29°, b.p. 240°, is formed from α-bromo-hexahydro-benzoic acid and from $\Delta^{4,6}$-dihydro-benzoic acid. Also from Δ^2-tetrahydro benzoic acid by boiling with alcoholic potash (B. **33**, 3455).

Δ^2-Tetrahydro-benzoic acid, *benzoleïnic acid* $CH_2\langle\begin{matrix}CH=CH\\ CH_2—CH_2\end{matrix}\rangle CH.CO_2H$, is a liquid boiling at 234° (A. **271**, 234; B. **27**, 2471). It is formed from benzoic acid.

Δ^3-Tetrahydro-benzoic acid $CH\langle\begin{matrix}CH—CH_2\\ CH_2—CH_2\end{matrix}\rangle CHCOOH$, m.p. about 13°, b.p. 237°, from 3- and 4-bromo-cyclo-hexane-carboxylic acid, and by the action of CO_2 and Mg upon Δ^3-bromo-cyclo-hexene (C. 1907, I. 1408; B. **43**, 1039).

Of the **tetrahydro-toluic acids,** the following seven are known, which are all obtained from the various bromo-methyl-cyclo-hexane-carboxylic acids by HBr, regenerative by means of quinolin, pyridin, etc. :

Δ^1-Tetrahydro-o-toluic acid	$CH_2—CH_2—C.CH_3$ $CH_2—CH_2—C.CO_2H$	m.p. 87°.[1]	
Δ^1-Tetrahydro-m-toluic acid	$CH_2.CH(CH_3).CH$ $CH_2—CH_2—C.CO_2H$	liquid	b.p.$_{11}$ 150°.[2]
Δ^2-Tetrahydro-m-toluic acid	$CH_2.C(CH_3)=CH$ $CH_2—CH_2—CH.CO_2H$	„	b.p.$_{20}$ 141°.[3]
Δ^3-Tetrahydro-m-toluic acid	$CH:C(CH_3)—CH_2$ $CH_2—CH_2—CH.CO_2H$	„	b.p.$_{100}$ 185°.[4]
Δ^4-Tetrahydro-m-toluic acid	$CH_2.CH(CH_3).CH_2$ $CH_2—CH=C.CO_2H$	m.p. 59°.[5]	
Δ^1-Tetrahydro-p-toluic acid	$CH_2CH—CH_2—CH$ $CH_2—CH_2—C.CO_2H$	m.p. 133°.[6]	
Δ^3-Tetrahydro-p-toluic acid	$CH_2C=CH—CH_2$ $CH_2—CH_2—CH.CO_2H$	m.p. 99°.[7]	

[1] C. 1905, II. 766. [2] C. 1905, II. 767. [3] C. 1907, I. 1409. [4] C. 1909, I. 172; [5] C. 1905, II. 767. [6] A. **280**, 159; C. 1906, II. 342. [7] C. 1909, I. 170.

The Δ^1- and Δ^2-tetrahydro-p-toluic acids and the Δ^2-tetrahydro-m-toluic acid have been split up into their optically active constituents by means of their brucin and strychnin salts. Starting from Δ^2-tetrahydro-m-toluic acid, *sylvestrene* and *carvestrene* (*q.v.*) have been built up, and, starting from Δ^3-tetrahydro-toluic acid, *α-terpineol* and *dipentene* (see below) (Perkin, jun.). **Δ^1-Tetrahydro-2, 6-xylylic acid,** m.p. 90° (C. 1899, II. 387).

α-**Cyclo-geranic acid,** 2, 6, 6-*trimethyl-Δ^2-tetrahydro-benzoic acid* $CH_2\langle\begin{matrix}CH{=}C(CH_3)\\CH_2{-}C(CH_3)_2\end{matrix}\rangle CHCO_2H$, m.p. 106°, b.p.$_{11}$ 138°, is formed, together with the isomeric *β*-**cyclo-geranic acid,** m.p. 94°, from geranic acid with concentrated sulphuric acid; its constitution is proved by its disintegration into *α*-acetyl-dimethyl-adipinic ester acid, and *ββ*-dimethyl-adipinic acid (B. **31,** 828, 881; **33,** 3713). **Δ^3-Cyclo-geranic acid,** 2, 6, 6-*trimethyl-Δ^3-tetrahydro-benzoic acid,* m.p. (*α*) 76°, (*β*) 84°, from oxy-dihydro-cyclo-geranic acid, used for preparing Δ^3-cyclo-citral (B. **41,** 2066). From the cyano-hydrin of dihydro-iso-aceto-phorone we obtain by saponification and elimination of H_2O, a **3, 3, 5-trimethyl-tetrahydro-benzoic acid,** m.p. 140°, b.p.$_{16}$ 154° (C. 1903, I. 1245).

Dihydro-benzoic Acids.—**$\Delta^{1,2}$-Dihydro-benzoic acid** $CH\langle\begin{matrix}CH.CH\\CH_2.CH_2\end{matrix}\rangle C.CO_2H$, m.p. 94°, is produced in the oxidation of *dihydro-benzaldehyde,* boiling at 121°–122°, with silver oxide. A different *dihydro-benzoic acid,* melting at 73°, is obtained from Δ_2-tetrahydro-benzoic acid dibromide (B. **24,** 2622). **Dihydro-cumic acid,** *p-iso-propyl-dihydro-benzoic acid* $C_6H_6(C_3H_7)COOH$, m.p. 130°–133°, is formed when nopic acid, an oxidation product of *β*-pinene, is boiled with sulphuric acid (B. **29,** 1926).

Hexa-, Tetra-, and Dihydro-phenyl Aliphatic Acids. **Hexahydro-phenyl-acetic acid** $C_6H_{11}.CH_2.COOH$, m.p. 33°, b.p. 244°, from cyclo-hexyl-malonic acid or from hexahydro-benzyl chloride and iodide with Mg and CO_2 (B. **40,** 2067). **Hexahydro-phenyl-propionic acid** $C_6H_{11}.CH_2.CH_2COOH$, b.p.$_{11}$ 143°, from hexahydro-benzyl-malonic acid. Amide, m.p. 120° (B. **41,** 2676).

Tetrahydro-phenyl fatty acids are formed by detaching water from the corresponding 1, 1-cyclo-hexanol fatty acids, or their esters, obtained by the action of bromo-aliphatic esters and zinc upon cyclo-hexanones. According to the dehydrating agents used, whether P_2O_5 and $HKSO_4$ or acetic anhydride, we obtain either the ring-unsaturated cyclo-hexene fatty acids or the isomeric cyclo-hexylidene fatty acids, with semi-cyclic double-binding:

$$CH_2\langle\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH_2\end{matrix}\rangle C{:}CH.CO_2H \xleftarrow{(CH_3.CO)_2O} CH_2\langle\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH_2\end{matrix}\rangle C\langle\begin{matrix}OH\\CH_2CO_2H\end{matrix}$$

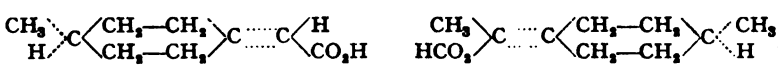
$$\overset{SO_4HK}{\underset{P_2O_5}{\downarrow}}\ CH_2\langle\begin{matrix}CH_2{-}CH\\CH_2{-}CH_2\end{matrix}\rangle C.CH_2CO_2H.$$

On heating, *both* series of acids split off CO_2, and change into alkylidene-cyclo-hexanes (A. **365,** 255).

From the easily synthesised cyclo-hexenones we immediately obtain with zinc and bromo-acetic ester, instead of oxy-acids, cyclo-hexadiene-carboxylic acids, which probably contain both double linkings in the ring, and which, on heating, split off CO_2 and yield dihydro-benzol derivatives (A. **323,** 136).

Δ^1-Cyclo-hexene-acetic acid, m.p. 38°, on oxidation with $KMnO_4$, probably forms first an aldehyde-ketonic acid Δ^1-acetyl-cyclo-pentene (B. **42**, 145), and then **Δ^2-cyclo-hexene-acetic acid,** m.p. 12°; see C. 1909, II. 2146. **4-Methyl-Δ^1-cyclo-hexene-acetic acid,** m.p. 42° (C. 1909, I. 286). **Δ^1-Cyclo-hexene-iso-butyric acid,** m.p. 72°.

Cyclo-hexylidene-acetic acid $(CH_2)_5 : C : CH.CO_2H$, m.p. 92°. The **4-methyl-cyclo-hexylidene-acetic acid,** m.p. 66° (inactive), has a special theoretical interest, since, without containing an unsym. carbon atom, it can be split up, by means of its brucin salts, into two optically active, mirror-isomeric acids, m.p. 52°, $[\alpha]_D = +81°$. The acids owe their optical activity to the existence of an enantiotropic molecular structure. In fact, the molecule of 4-methyl-cyclo-hexylidene-acetic acid,



in which the links in the plane of the paper are indicated by solid lines, and the links at right angles to the paper by dotted lines, contains no plane of symmetry; in other words, object and mirror image can be brought to coincide (A. **371**, 180; cp. also Vol. I.).

1, 3-Methyl-cyclo-hexadiene-acetic acid $CH_3C_6H_6CH_2CO_2H$, m.p. 171°, from 3-methyl-cyclo-hexenone.

1, 3, 5-Dimethyl-cyclo-hexadiene-acetic acid $(CH_3)_2C_6H_5CH_2CO_2H$, m.p. 151°, b.p.$_{15}$ 170°, from 3, 5-dimethyl-cyclo-hexenone.

Addendum.—Hexahydro-phenyl-acetylene-carboxylic acids:

Hexahydro-phenyl-propiolic acid $C_6H_{11}C : C.CO_2H$, b.p.$_{16}$ 139°, from hexahydro-phenyl-acetylene sodium and CO_2 (C. 1909, II. 208). **Hexahydro-phenyl-tetrolic acid** $C_6H_{11}.CH_2.C : CO_2H$, m.p. 75°, from cyclo-hexyl-allylene (C. 1910, II. 387).

Hexahydro-oxy-benzoic Acids.—**α-Oxy-cyclo-hexane-carboxylic acid, α-oxy-hexahydro-benzoic acid,** *cyclo-hexanol-1-carboxylic acid* $CH_2\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle C\langle\begin{matrix}CO_2H\\OH\end{matrix}$, melting at 106°, is formed when cyclo-hexanone, in ether, is treated with prussic and hydrochloric acids (C. 1909, II. 1869). α-Oxy-3-methyl-cyclo-hexane-carboxylic acid, b.p.$_{12}$ 164°; see C. 1907, I. 1407. 2-, 3-, and 4-Oxy-cyclo-hexane-carboxylic acids are formed by reduction of the oxy-benzoic acids or the cyclo-hexane-carboxylic acids with sodium and alcohol. They usually occur in cis-trans-isomeric forms, out of which the cis-forms of 3- and 4-oxy-cyclo-hexane-carboxylic acids pass easily into lactones with elimination of water.

Hexahydro-salicylic acid, (β-) *hexahydro-o-oxy-benzoic acid* $CH_2\langle\begin{matrix}CH_2.CH(OH)\\CH_2.CH_2—\end{matrix}\rangle CH.CO_2H$, m.p. 111°, results when nitrous acid acts upon hexahydro-anthranilic acid and by reducing β-keto-hexamethylene-carboxylic ester (B. **27**, 2472, 2476).

Hexahydro-m-oxy-benzoic acid, m.p. cis- 132°, trans- 120°, is obtained by the reduction of m-oxy-benzoic acid with sodium in ethyl alcohol (B. **29**, R. 549; C. 1907, I. 1408).

Hexahydro-p-oxy-benzoic acid, m.p. 121°, from 1, 4-cyclo-hexanone-carboxylic acid (C. 1904, I. 1082).

2-, 4-, 5-, and **6-Methyl-3-oxy-cyclo-hexanone-carboxylic acids** have been obtained from the corresponding oxy-toluic acids (C. 1910, I. 270).

3-Methyl-oxy-cyclo-hexane-carboxylic acids, cis- m.p. 140°, trans- m.p. 116°, from the corresponding ketonic acids (C. 1909, I. 172).

4-Methyl-4-oxy-cyclo-hexane-carboxylic acids, m.p. 153°, lactone m.p. 70°, from 1, 4-cyclo-hexanone-carboxylic ester and CH_3MgI (C. 1904, I. 1604).

Oxy-dihydro-cyclo-geranic acid, *δ-oxy-cyclo-geraniolane-carboxylic acid* $CH(OH)\begin{cases}CH_2—CH(CH_3)\\ CH_2—C(CH_3)_2\end{cases}CH.CO_2H$, cis- (*α*) m.p. 145°, trans- (*α*) m.p. 155°, lactone m.p. 58°, cis- (*β*) m.p. 158°, trans- (*β*) m.p. 38°, is formed in two stereo-isomeric pairs each by reduction of iso-phorone-carboxylic ester with Na and alcohol. By the action of dehydrating agents, all of these pass, more or less easily, into Δ^3-cyclo-geranic acid (A. **366,** 151).

3, 5, 5-Trimethyl-hexahydro-salicylic acid, m.p. 180°, b.p.$_{10}$ 204°, from trimethyl-*β*-keto-hexamethylene-carboxylic acid (C. 1903, II. 78).

Hexahydro-dioxy-benzoic acid is obtained from Δ^1-tetrahydro-benzoic dibromide (A. **271,** 280).

Dihydro-shikimic acid, *hexahydro-trioxy-benzoic acid* $(HO)_3C_6H_8.CO_2H$, m.p. 175°, results when shikimic acid is reduced with sodium amalgam.

Quinic acid, *hexahydro-tetraoxy-benzoic acid* $(HO)_4.C_6H_7.CO_2H$, m.p. 162°, optically active, is present in cinchona bark, in coffee beans, in bilberry, and, in small quantities, in hay and sugar-beet. It is obtained as a secondary product in the preparation of quinine, by extracting the quinia bark. When its calcium salt has been purified by recrystallisation, the acid is liberated by oxalic acid. Upon distillation, the acid breaks down into phenol, hydroquinone, benzoic acid, and salicyl-aldehyde. When boiled with water and lead peroxide it changes to hydroquinone, while manganese peroxide and sulphuric acid convert it into quinone. Proto-catechuic acid is formed when it is melted with caustic potash or soda. Ferments decompose calcium quinate into proto-catechuic acid. If air is excluded while the fermentation takes place, the products are formic acid, acetic acid, and propionic acid. Quinic acid is reduced by hydriodic acid to benzoic acid. The **calcium salt** has the formula $(C_7H_{11}O_6)_2Ca+10H_2O$. The **methyl ester,** m.p. 120°. **Amide,** m.p. 132°. **Tetracetyl-ethyl ester** $C_6H_7(O.COCH_3)_4.CO_2C_2H_5$ melts at 135° (B. **22,** 1462).

Inactive quinic acid is produced when its lactone, quinide, is boiled with milk of lime. **Calcium salt** $(C_7H_{11}O_6)_2Ca+4H_2O$.

Quinide $C_7H_{10}O_5$, m.p. 198°, optically inactive, results upon heating ordinary optically active quinic acid to 220°–240° (B. **24,** 1296).

Dioxy-dihydro-shikimic acid, *hexahydro-pentaoxy-benzoic acid* $(HO)_5C_6H_6.CO_2H$, melts at 156° with the elimination of water. It is optically inactive, and is obtained from the bromo-lactone, melting at 235°, which is formed in the action of baryta water (B. **24,** 1294) upon dibromo-shikimic acid.

Shikimic acid, *trioxy-tetrahydro-benzoic acid* $(HO)_3C_6H_6.CO_2H$, m.p. 184°, occurs in the fruit of *Illicium religiosum*. Its transposition products, dihydro- and dioxy-dihydro-shikimic acids, have been previously described.

Hexahydro-oxy-phenyl Fatty Acids.—**1, 1-Cyclo-hexanol-acetic acid** $C_5H_{10}:C(OH).CH_2CO_2H$, m.p. 63°. **1, 4-Methyl-cyclo-hexanol-acetic**

acid $CH_3.C_5H_9 : C(OH).CH_2.CO_2H$, α-acid, m.p. 141°, β-acid, m.p. 90°. **1, 4-Methyl-cyclo-hexanol-propionic acid** $CH_3.C_5H_9 : C(OH).CH(CH_3).CO_2H$, m.p. 110°. These esters are produced by condensation of cyclo-hexanones with bromo-aliphatic esters and zinc (A. **360**, 26; **365**, 261).

Hexahydro-mandelic acid $C_6H_{11}.CH(OH).COOH$, m.p. 166°, from hexahydro-phenyl-acetaldehyde-cyano-hydrin (B. **41**, 2677).

Cyclo-hexyl-glycidic esters like $[CH_2]_5 : \overset{\frown}{C.O.CH}.CO_2C_2H_5$, b.p.$_{17}$ 128°, and $[CH_2]_5 : \overset{\frown}{C.O.C}(CH_3)CO_2C_2H_5$, b.p.$_{40}$ 155°, are formed by condensation on cyclo-hexanones and chloracetic esters or chloro-propionic ester with sodium ethylate.

The glycidic acids produced by saponification easily break up into CO_2 and aldehydes or ketones (C. 1906, I. 1423; 1907, II. 332).

Keto-hydro-monocarboxylic Acids, 1, 2-cyclo-hexanone-carboxylic acids and their esters are produced (1) by cyclic aceto-acetic-ester condensation of pimelinic ester and its alkyl-substitution products by means of sodium (A. **317**, 27); (2) from cyclo-hexanone oxalic esters, the condensation products of the cyclo-hexanones with oxalic ester, on heating with rejection of carbon monoxide (A. **350**, 211); (3) by the action of sodium amide and CO_2 upon cyclo-hexanones in ether solution (C. 1910, II. 1378).

1, 2-Cyclo-hexanone-carboxylic acid $CH_2\langle\begin{matrix}CH_2—CO\\CH_2—CH_2\end{matrix}\rangle CH.CO_2H$, m.p. 80°, with rejection of CO_2. The ethyl ester boils at 107° (11 mm.), and is formed by the above methods. Like the β-keto-pentamethylene-carboxylic ester, it is a cyclic analogue of aceto-acetic ester. It is broken up by dilute sulphuric acid into cyclo-hexanone, and by boiling with alcoholic potash into pimelinic acid. With sodium alcoholate and methyl iodide it gives **1-methyl-1, 2-cyclo-hexanone-carboxylic ester**, b.p. 108°. It is split up by alcoholic potash to α-methyl-pimelinic acid; with ammonia the 1, 2-cyclo-hexanone-carboxylic ester produces tetrahydro-anthranilic ester $C_6H_8(NH_2)CO_2R$, m.p. 74° (A. **317**, 93). Special interest attaches to the **4-methyl-1, 2-cyclo-hexanone-carboxylic ester** $CH_3.CH\langle\begin{matrix}CH_2—CH_2\\CH_2—CO\end{matrix}\rangle CHCO_2C_2H_5$, b.p.$_{13}$ 123°, from β-methyl-pimelinic ester or 1, 3-methyl-cyclo-hexanone-oxalic ester; with sodium and iso-propyl iodide it gives **4-methyl-1-iso-propyl-1, 2-cyclo-hexanone-carboxylic ester** $CH_3CH\langle\begin{matrix}CH_2—CH_2\\CH_2—CO\end{matrix}\rangle C\langle\begin{matrix}C_3H_7\\CO_2C_2H_5\end{matrix}$, b.p.$_{14}$ 146°, from which, by saponification with dilute sulphuric acid, *methone* is formed (A. **342**, 198).

3, 5, 5-Trimethyl-1, 2-cyclo-hexanone-carboxylic acid, m.p. 111° with decomposition, is formed from dihydro-iso-aceto-phorone by treatment with CO_2 and Na in ether (C. 1902, II. 1372).

1, 3-Cyclo-hexanone-carboxylic acid $CH_2\langle\begin{matrix}CO.CH_2\\CH_2.CH_2\end{matrix}\rangle CH.CO_2H$, m.p. 74°, from tetrahydroxy-terephthalic acid by heating to 115° or by boiling with water, or by oxidation of m-oxy-hexahydro-benzoic acid in the form of its ester with sodium bichromate (B. **29**, R. 550; C. 1910, I. 533).

1, 4-Cyclo-hexanone-carboxylic acid $CO\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle CH.CO_2H + H_2O$,

m.p. 68°, is formed synthetically by the action of acetic anhydride upon α, γ, ϵ-pentane-tricarboxylic acid and subsequent distillation. The acid is useful as a starting-point for the synthesis of α-terpineol and dipentene (C. 1904, I. 1082). **3-Methyl-1, 4-cyclo-hexanone-carboxylic acid,** m.p. 94°; see C. 1909, I. 172.

Numerous γ-keto-carboxylic acids have been obtained by reducing the corresponding 1, 4-cyclo-hexanone-carboxylic esters with hydrogen and colloidal palladium (B. **42,** 1627). **2-Methyl-1, 4-cyclo-hexanone-carboxylic ethyl ester,** b.p.$_{15}$ 128°, **dihydro-iso-phorone-carboxylic ester,** occurs in two cis-trans-isomeric forms: α-form, m.p. 44°, b.p.$_{9}$ 125°; β-form, liquid, b.p.$_{12}$ 137°; and the free acids, α-form, m.p. 127°, β-form, m.p. 119°, are produced by oxidation of the oxy-dihydro-cyclo-geranic acids, passing into the trans-forms of these acids, by reduction with sodium and alcohol.

1-Acetyl-cyclo-hexane-carboxylic ester $CH_2\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle C\langle\begin{matrix}COCH_3\\CO_2C_2H_5\end{matrix}$, b.p. 241°–245°, is formed from 1, 5-dibromo-pentane and sodium aceto-acetic ester; on boiling with alcoholic potash it yields hexahydro-aceto-phenone (B. **40,** 3945). Similarly, we obtain **2-methyl-1-acetyl-cyclo-hexane-carboxylic ester** from 1, 5-dibromo-hexane and sodium aceto-acetic ester (B. **21,** 737).

Hexahydro-benzoyl-acetic ester $C_6H_{11}.CO.CH_2.CO_2C_2H_5$, b.p.$_{18}$ 136°, from hexahydro-benzoic ester, acetic ester and sodium (C. 1908, II. 1687).

Cyclo-hexyl-aceto-acetic ester $C_6H_{11}CH(COCH_3)CO_2C_2H_5$, b.p.$_{14}$ 126°, obtained in small quantities from iodo-cyclo-hexane and sodium-aceto-acetic ester (B. **42,** 2232).

Δ^6-1, 2-Cyclo-hexenone-carboxylic acid, *dihydro-salicylic acid* $CH_2\langle\begin{matrix}CH_2—CO\\CH_2—CH\end{matrix}\rangle C.CO_2H$, m.p. 128°, its ethyl ester, b.p.$_{12}$ 103°, from 1, 2-cyclo-hexanone-carboxylic ester by bromination and rejection of HBr from α-bromo-1, 2-cyclo-hexanone-carboxylic ester, b.p.$_{13}$ 144°, by boiling with aniline. On heating with soda-lime the acid breaks up into CO_2 and Δ^2-cyclo-hexanone (*J. pr. Ch.* 2, **80,** 495).

Δ^2-1, 4-Cyclo-hexenone-carboxylic esters like $CO\langle\begin{matrix}CH=C—CH_3\\CH_2.CH_2\end{matrix}\rangle CH.CO_2R$ are obtained by the action of sodium ethylate upon alkylidene-bis-aceto-acetic ester with rejection of one carboxyl group. They contain the group of glutaconic ester (Vol. I.), and can therefore, like the latter, be alkylated with sodium alcoholate and alkyl iodide. The esters occur in a neutral form insoluble in alkali, and an acid form soluble in alkali. By means of sodium ethylate, the former may be transformed into the latter. Reduction with hydrogen and colloidal palladium produces 1, 4-cyclo-hexanone-carboxylic esters. The cyclo-hexenone-carboxylic acids easily break up into CO_2 and Δ^2-cyclo-hexenones.

2-Methyl-Δ^2-1, 4-cyclo-hexenone-carboxylic ester $CO\langle\begin{matrix}CH=C—CH_3\\CH_2.CH_2\end{matrix}\rangle CH.CO_2.C_2H_5$, b.p.$_{18}$ 155°, from methylene iodide, and sodium-aceto-acetic ester, or by the action of sodium ethylate upon methylene-bis-aceto-acetic ester (B. **30,** 639; **41,** 2943); by addition of bromine and rejection of 2HBr it yields o-methyl-p-oxy-benzoic acid (B. **38,** 969).

2, 6-Dimethyl-Δ^2-1, 4-cyclo-hexenone-carboxylic ester, b.p. 140°,

from ethylidene-bis-aceto-acetic ester (A. **342**, 344). **Iso-phorone-carboxylic ester** $CO\langle\begin{matrix}CH{=}C(CH_3)\\CH_2{-}C(CH_3)_2\end{matrix}\rangle CH.CO_2C_2H_5$, b.p.$_{10}$ 136°–140°, is formed by attaching sodium-aceto-acetic ester to iso-propylidene-aceto-acetic ester. On saponification, iso-phorone is produced; and, on reduction with sodium and alcohol, a mixture of various isomeric oxy-dihydro-cyclo-geranic acids.

4-Iso-propylidene-1, 2-cyclo-hexanone-carboxylic ester $\begin{matrix}CH_3\\CH_3\end{matrix}\rangle C:C\langle\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH\end{matrix}\rangle\begin{matrix}CO\\CO_2C_2H_5\end{matrix}$ has been obtained, by cyclic aceto-acetic ester condensation, from γ-iso-propylidene-pimelinic ester (C. 1907, II. 1976).

5, 5-Dimethyl-Δ^1-1, 3-cyclo-hexenone-acetic ester $(CH_3)_2C\langle\begin{matrix}CH_2{-}CO\\CH_2{-}C\end{matrix}\rangle\begin{matrix}CH\\CH_2CO_2C_2H_5\end{matrix}$, b.p.$_{22}$ 171°; see C. 1909, I. 853.

2. Hydro-aromatic Dicarboxylic Acids.

Hexahydro-dicarboxylic Acids.—These acids, depending upon the position of the carboxyl groups with reference to one another, show the behaviour of dialkyl-malonic acids, sym. dialkyl-succinic acids, sym. α-dialkyl-glutaric acids, and sym. α-dialkyl-adipic acids.

1, 1-Dicarboxylic ester and **2-methyl-cyclo-hexane-1, 1-dicarboxylic ester** have been made by the action of sodium-malonic ester upon pentamethylene bromide and methyl-pentamethylene bromide. The free acids, when heated, split off CO_2 and become hexahydro-benzoic acid and hexahydro-o-toluic acid. **2-Methyl-cyclo-hexane-1, 1-dicarboxylic acid** $CH_2\langle\begin{matrix}CH_2.CH(CH_3)\\CH_2.CH_2\end{matrix}\rangle C(CO_2H)_2$ melts at 147°. Cyclo-hexane-dicarboxylic acid and its esters appear not to have been isolated as yet (B. **21**, 735; **26**, 2246).

Cyclo-hexane-malonic acid ethyl ester $C_6H_{11}.CH(CO_2C_2H_5)_2$, b.p.$_{20}$ 164°, and **cyclo-hexyl-cyanic acid ester,** b.p.$_{23}$ 158°, are obtained in small quantity from bromo- and iodo-cyclo-hexane with sodium-malonic ester and cyan-acetic ester respectively.

Cyclo-hexyl-malonic acid, m.p. 177°, breaks up, on heating, into CO_2 and hexahydro-phenyl-acetic acid (C. 1905, II. 1430). **Hexahydro-benzyl-malonic ester** $C_6H_{11}.CH_2.CH(CO_2C_2H_5)_2$, b.p.$_{12}$ 145°–155°.

Hexahydro-phthalic Acids.—A. Baeyer's theory (B. **23**, R. 577), based upon the spatial representations of van Hoff as to the union of the C atoms, predicts the possibility of geometrically isomeric hexahydro-phthalic acids. The latter isomerism is due to the different positions occupied by the carboxyls relatively to the plane of the hexamethylene ring; hence the isomerides are termed *cis*- and *trans*-forms.

cis-Hexahydro-o-phthalic acid, 1, 2-*hexamethylene-dicarboxylic acid* $C_6H_{10}(CO_2H_2)$ melts at 192°, and its *anhydride* melts at 32° and boils at 145° (18 mm.); the **trans-hexahydro-o-phthalic acid** melts at 215°, and its *anhydride* at 140°. They are produced together when Δ^1-tetrahydro-o-phthalic acid is reduced. The trans-acid is also obtained by the oxidation of o-methylol-hexahydro-benzoic acid. The cis-acid is more soluble in water than the trans-acid. The anhydride of the latter is converted by continuous heating at 210°–220° into the anhydride of

the cis-acid (A. **258**, 214). The trans-acid has been broken up by means of its quinine salt into optically active components, d- and l-trans-hexahydro-phthalic acid $[\alpha]_{D_2}+18{\cdot}2°$ and $-18{\cdot}5°$, m.p. 179°–183°. Anhydride, m.p. 164° (B. **32**, 3046).

Hexahydro-iso-phthalic acids are produced in the reduction of iso-phthalic acid and when 1, 1, 3, 3-hexamethylene-tetracarboxylic acid is heated to 200°–220°. The calcium salt of the cis-acid is more sparingly soluble. The *cis-acid*, melting at 162°, when heated to 180° with hydrochloric acid, changes in part to the *trans-acid*, melting at 188°. Both acids, with acetyl chloride, yield the *acid anhydride*, melting at 119° (B. **26**, R. 721).

Hexahydro-terephthalic acids result on reducing the hydro-bromides of the tetrahydro-terephthalic acids in glacial acetic acid with zinc dust, as well as upon heating hexamethylene-1, 1, 4, 4-tetracarboxylic acid to 200°–220°. In the latter case the trans-acid, melting at 200°, predominates. The cis-acid, melting at 161°, is also converted into it when heated with hydrochloric acid to 180°. As regards solubility, these three pairs of hexahydro-phthalic acids reduce fumaric and maleïc acids. They are also convertible one into the other in like manner. They have also been distinguished, one from the other, as *maleinoid* and *fumaroid* modifications.

α-Bromo-substitution products of these acids have also been prepared from the acid chlorides, by treatment with bromine. Bromo-substituted hexahydro-carboxylic acids have also been obtained by the addition of hydrogen bromide and bromine to the corresponding tetra- and dihydro-carboxylic acids.

Hexahydro-homo-iso-phthalic acid $C_6H_{10}[1, 3](COOH)(CH_2COOH)$, m.p. 158°, by reduction of homo-iso-phthalic acid, gives, on distilling its calcium salt, a **dicyclic ketone** $CH_2\langle\begin{matrix}CH_2.CH\\CH_2.CH\end{matrix}\rangle\begin{matrix}CH_2\\CH_2\end{matrix}\rangle CO$ (?); cp. camphor (B. **36**, 3610).

Tetrahydro-dicarboxylic Acids, *Tetrahydro-o-phthalic Acids.*—Depending upon the point of double union there are, theoretically speaking, four structurally isomeric bodies. The two modifications in which neither of the two CO_2H-groups is attached to a doubly combined C atom permit of a stereo-isomeric modification of each.

Δ^1-Tetrahydro-o-phthalic acid $\begin{matrix}CH_2.CH_2.C.CO_2H\\|\quad\quad\quad|\\CH_2.CH_2.C.CO_2H\end{matrix}$, melting at 120°, and its **anhydride** at 74°, is formed when hydro-pyro-mellitic acid is distilled. Potassium permanganate decomposes it into adipic acid (A. **166**, 346; **258**, 203).

Δ^2-Tetrahydro-o-phthalic acid $\begin{matrix}CH_2.CH{=}C.CO_2H\\|\quad\quad\quad|\\CH_2{-}CH_2{-}CH.CO_2H\end{matrix}$, melting at 215°, and its anhydride at 78°, has been obtained by the decomposition of *sedanonic acid*, an o-valeryl-tetrahydro-benzoic acid obtained from celery oil (B. **30**, 503). It is also formed on boiling the Δ^1-acid with caustic potash, when the double union is shifted, and by the reduction of phthalic acid or $\Delta^{2,6}$-dihydro-phthalic acid together with **trans-Δ^4-tetrahydro-o-phthalic acid** $\begin{matrix}CH{-}CH_2{-}CH.CO_2H\\\|\quad\quad\quad|\\CH.CH_2.CH.CO_2H\end{matrix}$, melting at 216°, and its **anhydride** at 140°. Acetyl chloride separates it from Δ_2-acid.

This reagent converts it alone into its corresponding anhydride (A. **258**, 211).

cis-Δ^4-Tetrahydro-o-phthalic acid melts at 174°. It is produced when the $\Delta^{2,4}$-dihydro-acid is reduced, as well as from its **anhydride,** melting at 58°. The latter anhydride is formed when the anhydride of the trans-Δ^4-acid is heated (A. **269**, 202).

Tetrahydro-iso-phthalic Acids.—The three theoretically possible structure-isomeric acids are all known, one of them even occurring in a stereo-isomeric modification (C. 1905, I. 1320; II. 474).

Δ^1=Δ^2-Tetrahydro-iso-phthalic acid $\begin{matrix}HO_2C.C{=}{=}CH{-}CHCO_2H\\ CH_2{-}CH_2{-}CH_2\end{matrix}$, m.p. 168°, is obtained by the reduction of iso-phthalic acid with sodium amalgam at 45°. Its anhydride, m.p. 78°, is also formed from the Δ^3- and Δ^4-acid by heating with acetic anhydride.

Δ^3-Tetrahydro-iso-phthalic acid $\begin{matrix}HO_2C.C{-}{-}CH_2{-}CHCO_2.H\\ CH{-}CH_2{-}CH_2\end{matrix}$, m.p. 244°, from the Δ^2- and Δ^4-acid on boiling with concentrated potash.

cis-Δ^4-Tetrahydro-iso-phthalic acid $\begin{matrix}HO_2C.CH{-}CH_2{-}CH.CO_2H\\ CH{=}CH{-}{-}CH_2\end{matrix}$, m.p. 165°, is formed together with the Δ^2-acid by reducing iso-phthalic acid with sodium amalgam. On heating with HCl to 170°, it is converted into **trans-Δ^4-tetrahydro-iso-phthalic acid,** m.p. 226°.

Tetrahydro-terephthalic Acids are theoretically possible in two structurally isomeric forms, depending upon the position of the double union; one of these can occur in two stereo-isomeric modifications.

Δ^2-Tetrahydro-terephthalic acid $CO_2H.CH\begin{matrix}CH & =CH\\ CH_2{-}&{-}CH_2\end{matrix}CH.CO_2.H$ is produced in two isomeric modifications by the reduction of $\Delta^{1,3}$- and $\Delta^{1,5}$-dihydro-terephthalic acids. The *trans-acid* melts at about 300°. The *cis-acid* melts at 150°. The latter is much more readily soluble in water than the former. Potassium permanganate oxidises them to succinic acid. Boiling sodium hydrate changes the two acids, like $\beta\gamma$-hydro-muconic acid, into $\alpha\beta$-hydro-muconic acid.

Δ^1-Tetrahydro-terephthalic acid $CO_2H.CH\begin{matrix}CH_2{-}&CH\\ CH_2{-}&CH_2\end{matrix}C.CO_2H$ melts above 300° and sublimes (A. **258**, 7).

Dihydro-dicarboxylic Acids.—*Dihydro-o-phthalic acids* are possible, according to the position of the double union, in six structurally isomeric forms, one of which can occur in two stereo-isomeric modifications.

$\Delta^{1,4}$-Dihydro-o-phthalic acid $\begin{matrix}CH.CH_2.C.CO_2H\\ \|\quad\quad\|\\ CH.CH_2.C.CO_2H\end{matrix}$, melting at 153° (its **anhydride** at 134°), is produced on boiling $\Delta^{2,4}$-dihydro-phthalic acid with acetic anhydride (A. **269**, 204).

$\Delta^{2,4}$-Dihydro-o-phthalic acid $\begin{matrix}CH.CH_2.CH.CO_2H\\ \|\quad\quad|\\ CH.CH.C\ .\ CO_2H\end{matrix}$, melting at 179° (its **anhydride** at 103°), is produced when the acid is acted upon in the cold with acetic anhydride.

The acid is produced, further, on boiling $\Delta^{2,6}$-dihydro-o-phthalic acid dihydro-bromide with methyl-alcoholic potash.

$\Delta^{2,6}$-Dihydro-o-phthalic acid $\begin{matrix}CH_2.CH:C.CO_2H\\ |\quad\quad|\\ CH_2.CH:C.CO_2H\end{matrix}$ melts at 215°, and its *anhydride* at 83°. The acid results by reducing phthalic anhydride

with sodium amalgam in alkaline solution, and by boiling the $\Delta^{2,4}$- and $\Delta^{3,5}$-acid with sodium hydrate (see also B. **27,** 3185).

trans-$\Delta^{3,5}$-Dihydro-phthalic acid $\begin{matrix}CH:CH.CH.CO_2H\\ |\quad\quad\quad|\\ CH:CH.CH.CO_2H\end{matrix}$, melting at 210°, is produced by reducing phthalic anhydride with sodium amalgam in acetic acid solution. The acid has been split up into its optically active components by means of its strychnin salt. On passing into the $\Delta^{2,6}$-acid by boiling with sodium hydrate, or into the cis-$\Delta^{3,5}$-acid by heating with acetic anhydride, the optical activity disappears, the resulting acids containing no unsym. carbon atom (C. 1907, I. 565).

cis-$\Delta^{3,5}$-Dihydro-phthalic acid melts at 174°. Its *anhydride*, melting at 99°, is formed when the trans-$\Delta^{3,5}$-acid is acted upon with acetic anhydride.

Dihydro-terephthalic Acids.—Depending upon the points of double union, there are four possible structural isomerides. One of these, the $\Delta^{2,5}$-acid, appears in two stereo-isomeric forms. All the modifications are known.

$\Delta^{1,3}$-Dihydro-terephthalic acid $CO_2H.C\begin{matrix}CH.CH\\ CH_2.CH_2\end{matrix}C.CO_2H$ is produced on digesting α, α_1-dibromo-hexahydro-terephthalic acid and Δ^2-tetrahydro-terephthalic acid dibromide with alcoholic potash (A. **258,** 23). The *dimethyl ester* melts at 85°.

$\Delta^{1,4}$-Dihydro-terephthalic acid $CO_2H.C\begin{matrix}CH.CH_2\\ CH_2.CH\end{matrix}C.CO_2H$ is formed by reducing terephthalic acid with sodium amalgam, by boiling the isomeric dihydro-terephthalic acids with sodium hydrate (A. **251,** 272), and by reducing p-dichloro-$\Delta^{1,4}$-dihydro-terephthalic acid, the result of the action of PCl_5 upon succinyl-succinic ester, with sodium amalgam (B. **22,** 2122).

The *dimethyl ester* melts at 130°. It condenses by means of its CH_2 groups with oxalic ester and with benzaldehydes in the presence of sodium alcoholate to terephthalic acid derivatives: *phthalide-dicarboxylic acid*, the *lactone* of the acid $(HOOC)_2C_6H_3CH(OH)COOH$, and *benzyl-terephthalic acid* $(HOOC)_2C_6H_3CH_2C_6H_5$ (B. **36,** 842).

$\Delta^{1,5}$-Dihydro-terephthalic acid results on boiling trans-$\Delta^{2,5}$-dihydro-terephthalic acid with sodium hydroxide; the *dimethyl ester* resinifies on exposure to the air (A. **258,** 18).

$\Delta^{2,5}$-Dihydro-terephthalic acids $CO_2H.CH\begin{matrix}CH:CH\\ CH:CH\end{matrix}CH.CO_2H$, cis-acid and trans-acid, are formed in the reduction of terephthalic acid. See also $\Delta^{1,5}$-dihydro-terephthalic acid. The *trans-diphenyl ester* melts at 146°. The *cis-dimethyl ester* melts at 77° (A. **258,** 17). This ester breaks up into terephthalic and hexahydro-terephthalic esters, on heating in a CO_2 atmosphere in the presence of palladium black (B. **36,** 2857).

Oxy- and **keto-hydro-benzol-dicarboxylic Acids.**—**α-Oxy-hexahydro-iso-phthalic acid** $\begin{matrix}CH_2\diagup CH_2—CH_2\diagdown C\diagup CO_2H\\ CO_2H\diagdown CH—CH_2\diagup C\diagdown OH\end{matrix}$ is obtained from m-keto-hexahydro-benzoic acid by the action of prussic acid and hydrochloric acid (B. **22,** 2186; C. 1904, I. 1082).

m-Dioxy-hexahydro-iso-phthalic acid $CH_2\begin{matrix}CH_2—C(OH)\\ CH_2—C(OH)\end{matrix}\!\!>\!\!CH_2\begin{matrix}CO_2H\\ CO_2H\end{matrix}$

melts with decomposition at 217°. Its *anhydride* melts at 175°. The acid is obtained from its nitrile, the product of the addition of prussic acid to dihydro-resorcinol (A. **278**, 49).

α,α_1-Dioxy-hexahydro-terephthalic acid $\begin{matrix}CO_2H\\HO\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\!>\!C\!<\!\begin{matrix}CO_2H\\OH\end{matrix}$ is formed when its dinitrile, melting with decomposition at 180°, is boiled. This dinitrile results on adding prussic acid to p-diketo-hexamethylene with hydrochloric acid (B. **22**, 2176).

Hexahydro-2, 5-dioxy-terephthalic acid $C_6H_8(OH)_2(COOH)_2$, ethyl ester, m.p. 136°, formed besides **tetrahydro-p-dioxy-terephthalic acid,** ester, b.p.$_{14}$ 219°, by reduction of succinyl-succinic ester with sodium amalgam. The dioxy-hexahydro-terephthalic ester, on distillation, partly splits off H_2O and passes into $\Delta^{1,4}$-dihydro-terephthalic acid ester (B. **33**, 390).

Δ^1-Tetrahydro-2-oxy-terephthalic acid, or *2-keto-hexamethylene*-1, 4-*dicarboxylic acid*

$$CO_2H.CH\!<\!\begin{matrix}CH_2.C(OH)\\CH_2.CH_2\end{matrix}\!\!>\!C.CO_2H, \text{ or } CO_2H.CH\!<\!\begin{matrix}CO—CH_2\\CH_2—CH_2\end{matrix}\!>\!CH.CO_2H$$

results from the reduction of oxy-terephthalic acid. When heated to 60° with water, it splits off carbon dioxide and becomes m-keto-hexahydro-benzoic acid, the oxime of which is obtained from tetrahydro-oxy-terephthalic acid by means of hydroxylamine hydrochloride (B. **22**, 2187).

Keto-tetrahydro-benzol-polycarboxylic esters and m-diketo-hexahydro-benzol-carboxylic esters, or hydro-resorcylic esters, have been prepared synthetically in great numbers from 1, 5-diketone- and δ-ketone-carboxylic esters, respectively, by the elimination of water or of alcohol. A series of keto-R-hexenes, dihydro-resorçins, tetrahydro-benzols, dihydro-benzols, etc., has been built up from these bodies as the foundation substances.

Several alkylidene-bis-aceto-acetic esters are to be regarded as cyclo-hexanolone-dicarboxylic esters.

Cyclo-hexanone-2, 4-dicarboxylic ethyl ester $CH_2\!<\!\begin{matrix}CO—CH\\CH_2—CH\end{matrix}\!\!>\!\begin{matrix}CH_2CO_2C_2H_5\\CH_2CO_2C_2H_5\end{matrix}$, b.p.$_{20}$ 180°, from pentane-α, γ, ϵ-tricarboxylic ester by cyclic aceto-acetic ester condensation (C. 1907, I. 344).

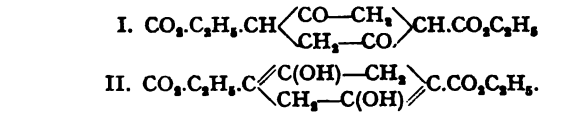
Cyclo-hexanone-2, 6-dicarboxylic methyl ester $CH_2\!<\!\begin{matrix}CH_2—CH\\CH_2—CH\end{matrix}\!\!>\!\begin{matrix}CO\\CO_2CH_3\end{matrix}\!\!>\!\begin{matrix}CO_2CH_3\\CO_2CH_3\end{matrix}$, keto-form melting at 125°, enol-form liquid from pentane-ω-tetracarboxylic ester, with sodium ethylate and elimination of carbonic acid ester (H. Meerwein). 2-Methyl-cyclo-hexanone-2, 6-dicarboxylic ethyl ester, b.p.$_{10}$ 160°, see A. **350**, 214.

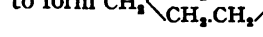
Succino-succinic acid $CO_2H.CH\!<\!\begin{matrix}CO.CH_2\\CH_2.CO\end{matrix}\!\!>\!CH.CO_2H$ results upon saponifying its diethyl ester with a calculated amount of normal sodium hydroxide, and by treating 2, 5-dioxy-terephthalic ester with sodium amalgam. The dry acid breaks down into two molecules of carbon dioxide and p-diketo-hexamethylene when heated to 200° (B. **22**, 2168).

Succino-succinic diethyl ester, m.p. 126°, is produced by the condensation of two molecules of succinic ester through the action of potassium, sodium, or sodium ethylate upon succinic ester (A. **211**,

306) or bromaceto-acetic ester (A. **245,** 74), as well as by the interaction of silver cyanide and iodo-aceto-acetic ester (A. **253,** 182), and by the reduction of 2, 5-dioxy-terephthalic ester with zinc and hydrochloric acid (B. **19,** 432).

Succino-succinic ester behaves like phloro-glucin. It also manifests many reactions of a ketone, corresponding to formula I. of 2, 5-diketo-hexamethylene-carboxylic ester; whereas it also conducts itself like a phenol, corresponding then to formula II. of 2, 5-dioxy-dihydro-terephthalic acid (B. **24,** 2692):



The ester crystallises in bright-green triclinic prisms, or colourless needles. It is insoluble in water, dissolves with difficulty in ether, very readily in alcohol; its solution shows a bright-blue fluorescence. Ferric chloride imparts a cherry-red colour to it. It dissolves in alkalies with a yellow colour, yielding metallic derivatives by the replacement of two hydrogen atoms. It does not unite with phenyl iso-cyanate, whereas the structurally similar β-keto-hexamethylene-carboxylic ester combines with it to form  (A. **317,** 104).

With hydroxylamine (in alkaline or acid solution) succino-succinic ester splits off CO_2 and yields **quinone-dioxime-carboxylic ester** $C_6H_2(N.OH)_2.CO_2R$, melting at 174° (B. **22,** 1283).

With phenyl-hydrazin it forms a phenyl-hydrazin derivative of dihydro-terephthalic acid (B. **24,** 2687; **26,** R. 590), while with hydrazin it yields *hexahydro-benzo-3, 4-dipyrazolone* (*q.v.*) (B. **27,** 472); with Am acetate, di-imino-succino-succinic ester, m.p. 178°, which is oxidised by Br to p-diamido-terephthalic ester (C. 1905, II. 1240).

If sodium-succino-succinic diethyl ester be treated with alkylene iodide, it yields the following compounds:

Diethyl-succino-succinic ester: *cis*-body is liquid; *trans*-body melts at 65°.

Di-n-propyl-succino-succinic ester: *cis*-body is liquid; *trans*-body melts at 86°.

Di-iso-propyl-succino-succinic ester: *cis*-body is liquid; *trans*-body melts at 116°.

Methyl-n- and **methyl-iso-propyl-succino-succinic ester** boil at 195°–200° (25 mm.).

p-Dichloro-hydroquinone-dicarboxylic ester $C_6Cl_2O_2(CO_2C_2H_5)_2$, melting at 195°, consists of yellowish-green crystals (B. **21,** 1761). When reduced with zinc dust and glacial acetic acid, it becomes **p-dichloro-hydroquinone-dicarboxylic ester** $C_6Cl_2H_2O_2(CO_2C_2H_5)_2$, crystallising in two different forms—colourless needles and yellow-green plates (B. **20,** 2796; **21,** 1759; **23,** 260). Similar behaviour is shown by dibromo- and di-iodo-hydroquinone-dicarboxylic esters (B. **32,** 1742). Compare the two forms of 2, 5-dioxy-terephthalic ester.

p-Dioxy-quinone-dicarboxylic ester $C_6O_2(OH)_2(CO_2C_2H_5)_2$, melting

at 151°, may be prepared by shaking dichloro-hydroquinone-dicarboxylic ester with sodium hydroxide, and by the action of nitrous acid upon dioxy-terephthalic ester (B. **19,** 2385). It crystallises in pale-yellow flakes and intense greenish-yellow prisms (B. **20,** 1307). It reacts acid, and forms salts with two equivalents of the metals. It does not form a dioxime with hydroxylamine, but an oxy-ammonium salt, and with phenyl-hydrazin a phenyl-hydrazin salt (B. **22,** 1290). Furthermore, it does not react with phenyl iso-cyanate (B. **23,** 265). Boiling hydrochloric acid decomposes the ester into carbon dioxide and dioxy-quinone. By the absorption of two atoms of hydrogen (by reduction with sulphurous acid) the ester becomes :

Tetroxy-terephthalic ester $C_6(OH)_4(CO_2R_2)$, or **dioxy-quinone-dihydro-carboxylic ester** $C_6H_2(O_2)(OH)_2(CO_2R)_2$. It crystallises in golden-yellow flakes, and melts at 178° (B. **20,** 2798). Its alkaline solution oxidises on exposure to the air (giving up two hydrogen atoms) to dioxy-quinone-dicarboxylic ester ; hence it yields the same products with hydroxylamine and phenyl-hydrazin (B. **22,** 1291). It forms a tetracarbanilido-derivative (B. **23,** 267) with four molecules of phenyl iso-cyanate.

Phloro-glucin-dicarboxylic ester $CH_2\langle\begin{matrix}CO—CH(CO_2C_2H_5)\\CO—CH(CO_2C_2H_5)\end{matrix}\rangle CO$, m.p. 104°, is formed by the condensation of three molecules sodium-malonic acid ester on heating to 120°–145°, with rejection of carbonic acid ester, with acetone-tricarboxylic ester as an intermediate product ; also by the condensation of acetone-dicarboxylic ester and malonic ester with sodium ethylate (B. **29,** R. 1117 ; **41,** 4171). It behaves like succino-succinic ester, dissolves without change in alkalies, and is coloured a cherry-red by ferric chloride. With acetic anhydride it forms a tri-acetyl derivative with hydroxylamine or trioxime (B. **21,** 176), with phenyl iso-cyanate or tricarbanilido-derivative (B. **37,** 4637). Fused with caustic potash, it forms phloro-glucin.

3. Hydro-benzol-tricarboxylic Acids.

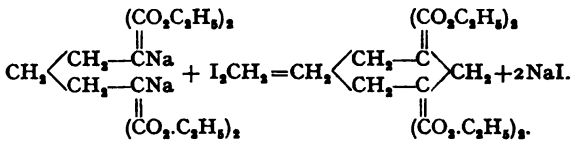
Among these we have the **dioxy-phenyl-acetic-dicarboxylic esters** $CO_2RCH\langle\begin{matrix}CO.C(CO_2R)\\CO.CH_2\end{matrix}\rangle CCH_2CO_2R$, condensation products of acetone-dicarboxylic ester (C. 1900, II. 963), and the analogous—

Dihydro-oxy-phenyl-acetic-dicarboxylic ester $CO_2C_2H_5.CH\langle\begin{matrix}CO—CH_2\\CH:C(CO_2C_2H_5)\end{matrix}\rangle CH.CH_2CO_2C_2H_5$, m.p. 82°, obtained by condensing glutaconic ester by means of sodium ethylate free from alcohol (B. **37,** 2113).

Dihydro-methyl-trimesinic acid $CH\langle\begin{matrix}C(COCH)=CH\\C(COOH)—CH_2\end{matrix}\rangle C\langle\begin{matrix}CH_3\\COOH\end{matrix}$ is formed from pyro-racemic acid by heating with sodium hydroxide. The acid is the intermediate product of the synthesis of uvitinic acid with pyro-racemic acid. On heating with concentrated sulphuric acid it splits off CO_2 and 2H, and passes completely into uvitinic acid ; on fusing it yields uvitinic acid besides **dihydro-uvitinic acid** $C_6H_5(CH_3)(COOH)_2$, m.p. 236°, and several tetrahydro-uvitinic acids. On reduction with Na amalgam we obtain **tetrahydro-methyl-trimesinic acid** $C_6H_6(CH_3)(COOH)_2$, m.p. 221° with decomposition (A. **305** 125).

4. Hydro-benzol-tetracarboxylic Acids.

Acids having two carboxyl groups attached to the same carbon atom have been obtained synthetically in the action of trimethylene bromide upon the disodium compound of methylene-dimalonic ester, as well as from the interaction of methylene iodide and disodium-trimethylene-dimalonic ester : hexamethylene-1, 1, 3, 3-tetracarboxylic ester, and from n-butane-tetracarboxylic ester with ethylene bromide : hexamethylene-1, 1, 4, 4-tetracarboxylic ester (Perkin, jun.) :



1, 1, 3, 3-Hexamethylene-tetracarboxylic acid decomposes at 220° with the elimination of $2CO_2$ into hexahydro-iso-phthalic acid (B. **25**, R. 159, 274).

Terpenes.

The *volatile* or *ethereal oils*, obtained mostly by the distillation of various plants (chiefly Coniferæ and Citrus species) with steam, more rarely by pressing them, or by extraction with volatile solvents or fats, contain, along with different compounds, certain hydrocarbons having the formula $C_{10}H_{16}$, which are called *terpenes*.

Terpenes $C_{10}H_{16}$, being the important, and often the chief, components of many ethereal oils of great value in perfumery, demand particular attention. They are more or less closely related to p-cymol or p-iso-propyl-methyl benzol, and a few to m-cymol.

Their classification, and the possibility of distinguishing the individual *true terpenes*, are mainly due to the painstaking researches of O. Wallach,* who has brought order and system out of this chaotic mass of hydrocarbons of the most varying origin.

The terpenes can be divided into two groups according to their behaviour. The first group contains the doubly unsaturated monocyclic terpenes, which can add four quadrivalent atoms, or atomic groups, and which can be regarded as true dihydro-p-cymols. To these belong limonene, dipentene, terpinolene, terpinene, and phellandrene. To these must be added sylvestrene and carvestrene, which also contain two double bindings, but are derived from m-cymol.

Terpenes of the second group are chiefly distinguished from these dihydro-cymols by adding only two univalent atoms or atomic groups, which indicates that they must contain a double carbon ring. The most important representatives of these bicyclic terpenes are camphene, pinene, fenchene, and sabinene. Some members of both groups are related to each other by transitional reactions. Completely saturated tricyclic terpenes have not been found up to the present among the ethereal oils. Quite recently terpenes of the formula $C_{10}H_{16}$ have become known, which contain no closed carbon chain, and are therefore distinguished from the real cyclic terpenes by calling them acyclic or olefinic terpenes (B. **24**, 682).

Beside the terpenes proper, we often find, among ethereal oils, hydro-

* O. Wallach, *Terpene und Campher*, Leipzig, 1909.

carbons of higher boiling-points, having the same percentage composition but a higher molecular weight. Among these we have the so-called *sesqui-terpenes* $C_{15}H_{24}$, the *di-terpenes* $C_{20}H_{32}$, and *poly-terpenes* $(C_5H_8)_x$. The same percentage composition is also shown by *isoprene* C_5H_8, generated by distillation of rubber and closely related to the terpenes, easily polymerised, *e.g.* into dipentene. Isoprene has therefore also been called hemi-terpene.

From the terpenes a large number of alcohols and ketones of the general composition $C_{10}H_{16}O$, $C_{10}H_{18}O$, and $C_{10}H_{20}O$ are derived. These are usually found besides the terpenes in the ethereal oils, and are comprised under the name "camphors," since the commercially important common, or Japanese, camphor is among them. Corresponding to the olefinic terpenes we have the olefinic camphors, and corresponding to sesqui-terpenes we have the sesqui-terpane camphors. We must therefore discuss the terpene alcohols and terpene ketones with their transformation products in connection with the terpenes and their addition products.

In the isolation of the terpenes the same difficulties are encountered as are met with in the preparation of dihydro-benzols. We nearly always obtain a mixture of closely related link-isomeric hydrocarbons, and it seems doubtful whether a perfectly uniform terpene has, as yet, been prepared. The elucidation of the constitution of the terpenes has, therefore, been a matter of special difficulty, but since the works of Baeyer, Perkin jun., Sellner, Wagner, and especially Wallach, have appeared, the structure of the majority of terpenes, and their relations to each other, appear to be settled. In many cases, as in dipentene, terpinene, sylvestrene, and carvestrene, a complete synthesis has been carried out, while in other cases, as in pinene, phellandrene, camphene, and fenchene, at least a partial synthesis has been effected. The isolation and the purification of the camphors are much easier. Many of them are distinguished by their ready crystallisation, while others may be easily regenerated in a pure state from characteristic derivatives. Here also the elucidation of the constitution has been followed by numerous total syntheses, *e.g.* camphor, menthone, α-terpineol, etc. The synthesis has here taken a step further, as also in some of the terpenes, by preparing new compounds, not yet found among ethereal oils, but closely related in their constitution and behaviour to the natural products, and thus creating new types of terpenes and camphors.

The question of the constitution of the sesqui-terpenes and poly-terpenes, as well as the oxygen-containing derivatives, is almost completely unsolved up to the present.

Properties.—The true terpenes, when pure, are colourless, strongly refracting liquids. Camphene alone is a solid. They boil, without decomposition, at 155°–180°. They are very volatile with steam, and have a pleasant odour. Many are optically active. Some, indeed, exist in two optically active forms with equal but opposite rotatory power. Dipentene is a racemic terpene.

Behaviour.—(1) Terpenes polymerise very readily. (2) Acids transpose many terpenes very easily into linkage-isomeric terpenes. (3) Many are oxidised by the oxygen of the air (compare α-pinene and β-phellandrene). They then manifest a tendency to resinify (see B. **29,**

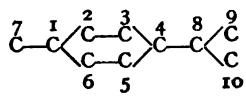
R. 658). The formation of benzene derivatives by oxidising terpenes is very important. Thus, turpentine oil with iodine yields p-cymol; with nitric acid, p-toluic acid and terephthalic acid. (4) The significance of the addition reactions for the classification of the terpenes has already been pointed out above :—(*a*) By addition of hydrogen the terpenes form hydro-terpenes (B. **36,** 1033). (*b*) The addition of chlorine and bromine, as well as of hydrogen haloids, in glacial acetic acid at low temperatures, gives rise to haloid hydro-terpenes. Some of these are well-crystallised compounds, which can be used for differentiating the terpenes. (*c*) Nitrosyl chloride NOCl (Tilden), or an alkyl nitrite, glacial acetic acid, and hydrochloric acid acting upon terpenes give rise to well-defined terpene nitroso-chlorides. With primary and secondary bases, these, usually unstable, nitroso-chlorides form stable terpene-nitrol-amines, or, with rejection of HCl, nitroso-terpenes, which are useful for characterisation. The latter make a transition from the terpenes to the terpene ketones (see Limonene nitroso-chloride). (*d*) Several terpenes unite with N_2O_4, forming nitrosates $C_{10}H_{16}(NO).O.NO_2$, and with N_2O_3, yielding nitrosites $C_{10}H_{16}(NO).O.NO$, or pseudo-nitrosites (nitrites) $C_{10}H_{16}(NO).NO_2$ (A. **332,** 313). The nitroso-chlorides, nitrosates, and nitrosites are bimolecular in the solid state, and should, therefore, be regarded as bis-nitroso-chlorides, bis-nitrosates and bis-nitrosites. In their transformations they behave as monomolecular compounds (B. **28,** 648; **29,** 10). (*e*) By the action of ozone the terpenes are converted into ozonides, while, with dilute $KMnO_4$ solution, they become glycols by attaching 2HO. Both reactions are important for determining the constitution of the terpenes.

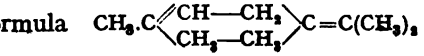
Concerning the addition of trichloro-acetic acid and formaldehyde to terpenes, see B. **29,** 695; **32,** 57.

Nomenclature.—In most cases camphor and the terpenes are designated by names derived from the plants in which they were first observed, and which contain them most abundantly in their ethereal oils. Since many terpenes, formerly considered uniform, have lately been found to be mixtures, the terpenes isolated from them have been distinguished from each other by prefixing Greek letters, *e.g.* α-, β-, and γ-terpinene.

Baeyer, observing the " Geneva nomenclature," suggested that the cyclic terpenes containing the same carbon skeleton as p-cymol, the dihydro-p-cymols, be called ***terpadienes***; then the tetrahydro-cymols would be ***terpenes***, and hexahydro-cymol ***terpane***. To obtain names for the terpenes which would be designated, according to this suggestion, as terpadienes, Wagner calls hexahydro-cymol ***menthane***, the tetrahydro-cymols ***menthenes***, and the dihydro-cymols or terpenes ***menthadienes*** (B. **27,** 1636, footnote).

The latter terminology has become most usual. In order to indicate the constitution of the dihydro-cymoles, the carbon atoms are designated by numbers :



The dihydro-cymol of the formula 

would be called $\Delta^{1,4,(8)}$-menthadiene, the dihydro-cymol $CH_3.C\begin{matrix}CH{-}CH_2\\ CH_2{-}CH\end{matrix}C.CH(CH_3)_2$, $\Delta^{1,4}$-menthadiene. The terpenes will be discussed in the following groups :—

A. Olefinic terpene or terpenogen group.
B. Monocyclic terpene or menthane group.
C. Bicyclic terpene groups.
  I. Sabinane or tanacetane group.
  II. Carane group.
  III. Pinane group.
  IV. Camphane group.
D. Sesqui-terpene and poly-terpene groups.

To the hydrocarbons of each group must be added the alcohols and ketones, the so-called camphors.

A. Olefinic Terpene or Terpenogen Group.

Many olefin hydrocarbons, alcohols, aldehydes, and acids with open carbon chain are included under this designation. They occur in ethereal oils, or in the transposition products obtained from the latter. They are distinguished chiefly by the fact that they, as a rule, are easily converted into hydro-aromatic, terpene-like, or aromatic substances.

1. *Olefinic Terpenes.*—**Myrcene,** b.p. 67° (20 mm.), sp. gr. 0·8025 (15°), n_D=1·4673, occurs with l-phellandrene and the aromatic phenols of the cinnamic series in bay oil. Its formula is $C_{10}H_{16}=(CH_3)_2C:CH.CH_2.CH_2C(:CH_2).CH:CH_2$ or $CH_2:C(CH_3).CH_2.CH_2.CH_2.C(:CH_2).CH:CH_2$, b.p.$_{20}$ 67°, D_{15} 0·8025. It is also found in the ethereal oil of *Lippia citriodora.* The terpene isolated from hop oil is also probably identical with myrcene (C. 1903, I. 1028).

Artificially, it is prepared by eliminating water from linalool (see below) by heating with $KHSO_4$. It adds 4 Br atoms. By reduction with sodium and alcohol we obtain **dihydro-myrcene** $C_{10}H_{18}$, b.p. 172°, tetrabromide, m.p. 88°, which is converted by glacial acetic-sulphuric acid into the isomeric cyclo-dihydro-myrcene (B. **34,** 3126). By heating under pressure to 300°, myrcene is polymerised to dimyrcene, b.p.$_{13}$ 160°–200°, and to undistillable poly-myrcenes; with N_2O_3 dimyrcene gives a nitrosite $(C_{10}H_{15}N_3O_7)_2$, apparently identical with the nitrosite of the same composition obtained from rubber (B. **35,** 3264).

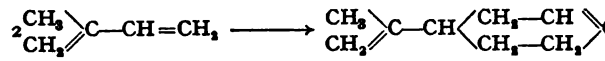
Ocimene $C_{10}H_{16}=(CH_3)_2C:CH.CH_2.CH:C(CH_3)CH:CH_2$ (?), b.p.$_{20}$ 81°, D_{15} 0·8031, has been obtained from the ethereal oil of *Ocimum basilicum.* It differs from myrcene only by the position of a double link, since sodium and alcohol reduce it to dihydro-myrcene with addition of two H atoms. On oxidation with ozone, we obtain, among other products, acetone, methyl-glyoxal, and malonic dialdehyde (C. 1907, II. 679; 1909, I. 373).

Anhydro-geraniol $C_{10}H_{16}$, b.p. 172°–176°, sp. gr. 0·8232 (20°), n_D=1·4835, is obtained by heating geraniol with potassium bisulphate to 170°. It can also take up six bromine atoms (B. **24,** 682). *Linalaolene* $C_{10}H_{18}$ boils at 165°–168°. Its specific gravity is 0·7882 (20°), n_D=1·455. It is formed in the reduction of *linalool* (B. **27,** 2520).

Isoprene C_5H_8, b.p. 37°, must be considered under the olefinic

terpenes or terpenogens. It is a distillation product from rubber. It may be obtained by conducting vapours of turpentine oil through tubes at a dull-red heat (A. 228). On its synthesis by disintegration of β-methyl-pyrrolidin, see this.

Isoprene very probably consists in the main of *methyl-divinyl*, $CH_3 \diagdown C(CH_2)-C=CH_2$. It can take up two molecules of hydrogen bromide, forming dimethyl-trimethylene bromide. It polymerises very readily to dipentene (*J. pr. Ch.* 2, **55**, 1; C. 1900, II. 331):



Under different conditions isoprene is polymerised to para-rubber.

2. *Olefinic Terpene Alcohols.*—**d-Citronellol** $C_{10}H_{22}O=CH_2 : C(CH_3)CH_2.CH_2.CH_2CH(CH_3)CH_2.CH_2OH$ (?), b.p.$_{15}$ 113°–114°, was first obtained by the reduction of d-citronellal; it is found native in Java citronel. It is a colourless oil, smelling agreeably of roses. Its constitution follows from its connection with d-citronellol. An alcohol very similar to d-citronellol, but lævo-rotatory, *l-citronellol*, l-rhodinol, is found, besides geraniol, in several species of rose, geranium, and pelargonium oils. It is probably link-isomeric with d-citronellol in the sense of the formula $(CH_3)_2C : CH.CH_2.CH_2CH(CH_3)CH_2CH_2OH$, since, on oxidation, it passes into an aldehyde isomeric with d-citronellal, viz. rhodinal. But the question of the constitution of the citronellols cannot be regarded as finally decided. An *i-citronellol*, i-rhodinol, b.p.$_{10}$ 110°, is formed by the reduction of the synthetic geranic acid (B. **29**, 923; **30**, 33; C. 1904, II. 440; vgl. B. **29**, R. 785).

Geraniol $C_{10}H_{18}O=(CH_3)_2C : CH.CH_2.CH_2.C(CH_3) : CH.CH_2OH$, b.p.$_{17}$ 120°–122°, forms the chief alcoholic constituent of *geranium oil*, rose oil, pelargonium oil, palma rose oil, etc., and is the most frequently occurring aliphatic terpene alcohol (B. **29**, R. 785); it yields a characteristic crystallised compound with calcium chloride, which can be employed for separating geraniol from ethereal oils. It is optically inactive, and has the same relation to citral as citronellol has to citronellal. The synthesis of geraniol is accomplished with that of citral. An alcohol probably stereo-isomeric with geraniol—

Nerol, b.p. 225°, D_{15} 0·880, has been found in the oils of neroli, petit grain, bergamot, and linaloe, partly in a free condition, partly esterified. It is distinguished from the otherwise very similar geraniol by its inability to form a solid calcium chloride compound, and by the formation of a crystalline tetrabromide, m.p. 119°. Geraniol and nerol probably stand to each other in the same relation as citral-a and citral-b, geraniol corresponding to the former, and nerol to the latter (B. **39**, 1780.)

l-Linalool, *licareol* $C_{10}H_{18}O=(CH_3)_2C : CH.CH_2.CH_2.C(CH_3)(OH).CH : CH_2$, b.p. 197°–199°, D_{20} 0·8702, $n_D=1·4695$, is found in linaloë oil from *Licari Kanali*, as well as *lavender*, bergamot, limette and origanum oil.

d-Linalool, coriandrol, is found in *coriander oil* and *oil of pomegranates* and *orange blossoms*. By reduction with Ni and hydrogen, geraniol and linalool, as well as ocimene, pass into 2, 6-dimethyl-octane, which proves that the same carbon frame forms the basis of

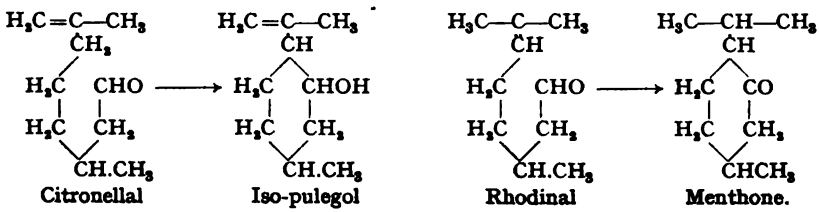
all these compounds. Dilute sulphuric acid converts the linalool with ease into inactive *terpin hydrate*; this conversion is made with greater difficulty with geraniol (B. **28**, 2137). Formic and glacial acetic-sulphuric acids convert geraniol with some difficulty, and the linalools with greater ease, into solid *α-terpineol*, m.p. 35°. In this process linalool is partly isomerised to geraniol, and, on the other hand, geraniol can be converted into inactive linalool (*J. pr. Ch.* 2, **60**, 244). Besides, or instead of, terpin hydrate and terpineol, terpenes, like terpinene, and terpinolene, are formed by stronger action of these agents. By the action of geraniol esters with concentrated acids cyclo-geraniol is formed, the alcohol corresponding to cyclo-citral (C. 1903, I. 266).

The constitution of these bodies, as well as that of the corresponding aldehydes and acids, has been mainly deduced from their conversion into *methyl-heptenone* $(CH_3)_2C : CH.CH_2.CH_2.CO.CH_3$, which has been previously described. Again, this methyl-heptenone has been employed in the synthesis of certain bodies belonging to this group. Thus by condensation with zinc and allyl iodide it yields **homo-linalool** $(CH_3)_2C : CH.CH_2.CH_2C(CH_3)OH.CH_2.CH : CH_2$, boiling at 102°–104° (14 mm.) (B. **29**, 693; cp. C. 1899, I. 24). α-Alkyl-geraniols are obtained from citral and alkyl-magnesium compounds (C. 1904, II. 624).

3. *Olefinic Terpene-aldehydes*—**Citronellal** $C_{10}H_{18}O=CH_2 : C(CH_3).CH_2.CH_2.CH_2.CH(CH_3).CH_2.CHO$ (I.) and $(CH_3)_2C : CH.CH_2.CH_2.CH(CH_3).CH_2CHO$ (II.), boiling at 205°, is optically dextro-rotatory. It is found in citronella oil, in the oil from *Eucalyptus maculata*, var. *citriodora*, etc. (B. **29**, 904). l-Citronellal has hitherto only been found in *Java lemon oil*. Acetic anhydride condenses it to *iso-pulegol*, a terpene alcohol very similar to, yet not identical with, pulegol, a reduction product obtained from pulegon (B. **30**, 22). It changes to d-citronellol upon reduction.

By oxidation with $KMnO_4$ the acetal of citronellal in aqueous solution is split up into acetone and the half-aldehyde of β-methyl-adipinic acid, whereas in acetone solution it is converted to the extent of 80 per cent. into a dioxy-aldehyde, which, on further oxidation with CrO_3, yields an oxy-dialdehyde and finally a **keto-aldehyde** $CH_3COCH_2.CH_2.CH_2CH(CH_3).CH_2CHO$ (B. **34**, 2981). Upon oxidation of the citronellal with ozone, acetone and β-methyl-adipinic acid are obtained, but not quantitatively. Natural citronellal, therefore, appears to be a mixture of two very similar aldehydes, which are link-isomeric in the sense of the above formula (B. **41**, 2187).

A lævo-rotatory aldehyde, *rhodinal*, closely related to citronellal, is formed by oxidation of citronellal. The formula (II.) above is ascribed to it. It differs from citronellal in that acetic anhydride does not change it into iso-pulegol, but into a cyclic ketone, *menthone*. The process may be represented by the following formulæ :—



The reverse of this process takes place on illuminating an aqueous-alcoholic solution of menthone. The ring is opened, and an unsaturated aldehyde similar to citronellal, but of lower b.p., 195°, is formed (B. **40,** 2421). It may be identical with the aldehyde designated as *mentho-citronellal*, obtained by splitting up menthone-oxime (A. **296,** 131).

Citral, *geranial* $C_{10}H_{16}O=(CH_3)_2C:CH.CH_2.CH_2.C(CH_3):CH.CHO$, b.p. 228°–229°, is a faint-yellow oil smelling of lemon. It is found in lemon oil, verbena oil, and particularly in lemon-grass oil (?), from which it is prepared industrially; also in many other ethereal oils; it is also formed by the oxidation of geraniol (C. 1908, I. 1375); synthetically, it can be prepared by the distillation of geranium acid and calcium formate (B. **31,** 827). The natural citral consists of two structurally identical stereo-isomeric forms, citral a and b, which can be separated by their different ease of condensation with cyano-acetic acid to **citralidene-cyano-acetic acids,** m.p. 122° and 95° (B. **33,** 877). With β-naphthylamine and pyro-racemic acid citral combines to form the characteristic **citryl-naphtho-cinchonic acid** (*q.v.*), m.p. 197° (B. **31,** 3195). Like cinnamic aldehyde, citral combines with sulphites not only to form the normal bisulphite compound with attachment of $2SO_3HNa$ to the olefin links, but also salts of **citral-dihydro-disulphonic acid** (B. **31,** 3278). By boiling with soda solution, citral is split up into methyl-heptenone and acetaldehyde (C. 1897, I. 495). It is oxidised by ozone to acetone, lævulinic aldehyde, or lævulinic acid and glyoxal (?) (B. **40,** 2823). By treatment with potassium bisulphate, HI, acetic acid, etc., it is converted into *cymol* with elimination of H_2O. But if citral derivatives, unconvertible into cymol, like citralidene-aniline (C. 1901, II. 716), citralidene-acetic acid, -cyano-acetic acid, -aceto-acetic ester, etc., are treated with concentrated H_2SO_4 or H_3PO_4, we obtain derivatives of *cyclo-citral*, a trimethyl-tetrahydro-benzaldehyde. Similarly, the so-called **pseudo-ionone** $(CH_3)_2C:CH.CH_2.CH_2.C(CH_3):CHCH:CHCOCH_3$, $b.p._{12}$ 143°–145°, obtained by the condensation of citral with acetone, forms a hydro-aromatic ketone called **ionone,** under the influence of concentrated H_2SO_4; cp. also cyclo-dihydro-myrcene (above), cyclo-geraniol, cyclo-geranic acid, and cyclo-geraniolene (above).

4. *Olefinic Terpene Acids.*—**Citronellic acid** (*rhodinic acid*, B. **29,** R. 352) $CH_2:C(CH_3).CH_2.CH_2.CH_2CH(CH_3)CH_2COOH$ and $(CH_3)_2C:CH.CH_2.CH_2CH(CH_3)CH_2COOH$, $b.p._{10}$ 143°–145°, obtained from its nitrile formed by withdrawing water from citronell-aldoxime, or by oxidation of citronellal, to which it can be restored by distilling its calcium salt with calcium formate. From geranic acid it is obtained by reduction with sodium and amyl alcohol (B. **31,** 2899).

Reduction of its ester with sodium and alcohol produces i-citronellol (see above), which proves the relation between the geraniol and citronellol series.

Geranic acid $(CH_3)_2C:CH.CH_2.CH_2C(CH_3):CHCOOH$, $b.p._{13}$ 153°, is also formed from citral. It has been prepared synthetically from methyl-heptenone with iodo-acetic ester and bromo-acetic ester and zinc (B. **29,** R. 222; **31,** 825). Sulphuric acid converts it into isomeric hydro-aromatic *cyclo-geranic acid*. By heating at ordinary pressures

geranic acid produces **geraniolene** C_9H_{16}, which is isomerised by sulphuric acid into cyclo-geraniolene (A. **324,** 101).

B. Monocyclic Terpene or Menthane Group.

To this group belong the terpenes limonene, dipentene, terpinolene, α-, β-, and γ-terpinene, α- and β-phellandrene, and the synthetic $\Delta^{2,4}$-menthadiene, which must all be regarded as dihydro-p-cymols, also sylvestrene and carvestrene, which must be regarded as dihydro-m-cymols. These terpenes are partly optically active, and partly inactive, or racemic. Numerous transitions and transformations connect the various terpenes, and several of them have been made by molecular synthesis.

1. *Limonene and Dipentene Group.*—

Limonene $C_{10}H_{16}=CH_3C\begin{matrix}\diagup\!\!\diagup CH\text{—}CH_2\\ \diagdown\!\!\diagdown CH_2\text{—}CH_2\end{matrix}\!\!>\!CH.C\begin{matrix}\diagup\!\!\diagup CH_2\\ \diagdown\!\!\diagdown CH_2\end{matrix}$ is known in three modifications—d-limonene, l-limonene, and [d+l]-limonene or dipentene.

d-Limonene, *citrene, hesperidene, carvene,* together with pinene, is among the most widely distributed terpenes. It is present in the oil obtained from the shell of *Citrus aurantium,* in lemon oil, in the oil of bergamot, in oil of dill, in oil of celery, etc. It boils at 175°; $[\alpha]_D=+106{\cdot}8°$. **l-Limonene** occurs in the oil of pine-needles, in oil of fir, and in oil of peppermint. It boils at 175°; $[\alpha]_D=-105°$. On the preparation of l-limonene from d-carvone, see B. **88,** 735.

Both limonenes are liquids, with an agreeable lemon-like odour. Their specific gravity equals 0·846 (20°). They differ from each other, as do their derivatives, almost entirely by their opposite rotatory power (A. **252,** 144). The two active limonenes combine with dry bromine to *tetrabromides* melting at 104°, and having equally large but opposite rotatory power of about $[\alpha]_D=73°$. The moist haloid acids change the optically active limonenes to addition products of [d+l]-limonene or dipentene.

On conducting dry HCl through a CS_2 solution of limonene, a monochlorohydrate is obtained which, on reduction with sodium and cold alcohol, gives carvo-menthene, and, on treating with dilute alkali and sodium acetate, optically active α-terpineol (B. **86,** 1036; A. **350,** 154).

By gentle oxidation with $KMnO_4$ limonene is converted into the quadrivalent alcohol $C_{10}H_{10}(OH)_4$. When the optically active limonenes are exposed to elevated temperatures they become dipentenes.

The nitroso-chlorides of the limonenes deserve particular attention (B. **28,** 1308; cp. also B. **29,** 10). d-Limonene forms two chemically identical nitroso-chlorides, with, however, different physical properties:

α, **d-** and **l-Limonene-nitroso-chloride,** m.p. 103°, $[\alpha]_D=\pm313°$.
β, **d-** and **l-Limonene-nitroso-chloride,** m.p. 105°, $[\alpha]_D=\pm240°$.

All the four nitroso-chlorides give, on heating with sodium methylate, carvoxime, m.p. 72°, l-limonene nitroso-chlorides giving d-carvoxime, and d-limonene-nitroso-chlorides l-carvoxime (cp. also B. **43,** 519).

[d+l]-Limonene, dipentene, *cinene,* sp. gr. 0·853 (B. **28,** 2145;

29, 4), boils at 175°. It is associated with cineol in *Oleum cinæ*. It is produced by heating d-limonene, l-limonene, pinene, and camphene to 250°–300°; it is, therefore, present in the Russian and Swedish turpentine oil, obtained by application of great heat. It is derived also from the distillation of rubber, and the polymerisation of the *isoprene* C_5H_8, formed simultaneously (A. **227**, 295). It is also produced on mixing equally large quantities of d- and l-limonenes, as well as when pinene is boiled with alcoholic sulphuric acid. It forms, too, on withdrawing water from linalool, terpine hydrate, terpineol, and cineol. By nuclear synthesis, dipentene is obtained from the synthetic α-terpineol by heating with potassium bisulphate (C. 1904, I. 1604).

It may be prepared pure by heating its hydrochloride with aniline or sodium acetate in glacial acetic acid solution.

Pure dipentene is a liquid with an agreeable odour of lemon.

Although more stable than most of the other terpenes, it can yet be changed into the isomeric terpinene by alcoholic sulphuric acid or hydrochloric acid. It is oxidised to p-cymol by concentrated sulphuric acid or phosphorus pentasulphide. p-Cymol is also obtained by treating its dihydro-bromide with bromine and reducing (B. **31**, 1402).

The derivatives of dipentene can be obtained not only from the dipentenes, but also by mixing the corresponding derivatives of dextro- and lævo-limonene.

trans-Dipentene-dihydro-chloride $C_{10}H_{16}.2HCl$ boils at 119° (10 mm.) and melts at 50°. **cis-Dipentene-dihydro-chloride,** m.p. about 22°.

The **trans-dipentene-dihydro-bromide** $C_{10}H_{16}.2HBr$, from d-limonene, dipentene, terpine, and cineol with hydro-bromic acid, melts at 64°.

cis-Dipentene-dihydro-bromide $C_{10}H_{16}.2HBr$, melting at 37°, results from the action of HBr upon a well-cooled solution of cineol in glacial acetic acid; see also cis-Terpine (B. **26**, 2864).

Tetrahydro-dipentene tribromide, *tribromo-terpane* $C_{10}H_{17}Br_3$, is derived from trans-dipentene dihydro-bromide by the action of bromine upon the glacial acetic acid solution (A. **264**, 25).

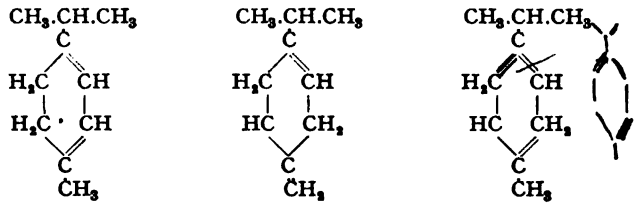
Dipentene tetrabromide $C_{10}H_{16}.Br_4$ melts at 124° (A. **281**, 140).

Dipentene dihydro-iodide $C_{10}H_{16}.2HI$ melts at 77°–79° (A. **239**, 13).

Dipentene nitroso-chloride $C_{10}H_{16}(NO)Cl$ melts at 102°; see Carvoxime, p. 510 (A. **270**, 175).

Terpinolene $CH_3.C\begin{matrix}CH—CH_2\\ CH_2—CH_2\end{matrix}\!\!>C=C<\begin{matrix}CH_3\\ CH_3\end{matrix}$, melting at 75° (14 mm.), has not yet been observed in ethereal oils. It is produced when terpine hydrate, terpineol, and cineol are boiled with dilute sulphuric acid, and by heating pinene with the concentrated acid. Boiling oxalic acid or anhydrous formic acid also liberate it from the terpineol melting at 35° (A. **275**, 106; **368**, 11); or anhydrous formic acid (A. **368**, 11) with bromine terpinolene forms a dibromide $C_{10}H_{16}Br_2$, m.p. 70° (B. **27**, 447), and a tetrabromide $C_{10}H_{16}Br_4$, m.p. 116°, from which it can be regenerated, in great purity, by reduction with zinc dust and alcohol (B. **42**, 4644). Halogen hydride is added to it with formation of dipentene dihalogenides. *Terpinolene* belongs to the most unstable terpenes, and is changed with especial ease by acids displacing the semicyclic double link into the nucleus and thus forming terpinene.

The Terpinene Group.—The name terpinene is used for designating the three following dihydro-cymols :



α-Terpinene β-Terpinene γ-Terpinene.

Of these, the α- and γ-terpinenes have been found in ethereal oils, while the β-terpinene has hitherto only been prepared synthetically. Both the natural terpinene and the terpinene artificially prepared from other terpenes or terpene alcohols represent a mixture of various amounts of α- and γ-terpinenes, in which α-terpinene usually predominates. The isolation of a perfectly pure α- or γ-terpinene has hitherto not been accomplished.

Terpinene (α+γ), b.p. 179°–181°, D 0·846 (20°) (B. **42**, 2425), when pure, has an odour resembling lemons and is optically inactive. It has been found in cardamom oil, elemi oil, coriander oil, ajowan oil, etc., of which the latter is particularly rich in γ-terpinene. It results on boiling dipentene, terpine, phellandrene, cineol, or dihydro-carveol with dilute alcoholic sulphuric acid, and when pinene is shaken with a little concentrated sulphuric acid. A partly pure γ-terpinene is obtained (1) from chloro-carvenene, the result of the action of PCl_5 upon carvenone, or by reduction of sodium and alcohol (B. **40**, 2471) ; (2) from carvenylamine by rejection of ammonia (B. **40**, 1256) ; (3) from methyl-dichloro-methyl-keto-dihydro-benzol, with iso-propyl-magnesium iodide, and heating the resulting compound with alcoholic potash (B. **42**, 2404, 4427). The last method of formation represents a complete nuclear synthesis of terpinene.

β-Terpinene, b.p. 173°–174°, specific gravity 0·838, has been obtained from the condensation product of sabina-ketone with brom-acetic ester and zinc by rejection of water and distillation of the resulting unsaturated acid, $C_9H_{14} : CHCO_2H$, m.p. 68°. It unites with bromine to form a crystallised tetrabromide, m.p. 155°, while α- and γ-terpinenes only yield liquid bromine addition products (A. **362**, 285).

All three terpinenes unite with two molecules of halogen hydride to form well-defined terpinene dihalogenides, from which, on heating with aniline or alcoholic potash, a mixture of α- and γ-terpinene is regenerated. On shaking up with dilute alkali, dihalogen hydrates are converted into terpinene-terpin and terpinenol (*q.v.*), compounds which are isomeric with the analogous conversion products of the dipentene halogenides, terpin and terpineol.

Especially characteristic of α-terpinene is the formation of **terpinene nitrosite** $C_{10}H_{16}(NO).O.NO$ or $C_{10}H_{15}(N.OH)O.NO$, m.p. 155°, formed by the action of potassium nitrite upon terpinene dissolved in glacial acetic acid, and used for discovering terpinene in ethereal oils. It is insoluble in alkali, but gives, with bases, nitrolamines soluble in alkali. With ammonia it thus gives **terpinene-nitrolamine** $C_{10}H_{15}$

(N.OH).NH_2, m.p. 118° (A. **241**, 320). With zinc dust the terpinene nitrosite and the nitrolamines are reduced to carvenone, while sodium and alcohol reduce them to tetrahydro-carvone and tetrahydro-carvyl-amine (B. **40**, 579).

On oxidation with potassium permanganate, α-terpinene yields **α, α_1-dioxy-α-methyl-α_1-iso-propyl-adipinic acid,** m.p. 189°, which can be further broken down to ω-dimethyl-acetonyl-acetone (A. **362**, 293):

$$\begin{matrix}CH_3—C(CH_3)=CH\\ CH_2—C(C_3H_7)=CH\end{matrix} \longrightarrow \begin{matrix}CH_3—C(CH_3)OH—CO_2H\\ CH_2—C(C_3H_7)OH—CO_2H\end{matrix} \longrightarrow \begin{matrix}CH_3—CO.CH_3\\ CH_2—CO.CH(CH_3)_2\end{matrix}$$

The isomeric γ-terpinene, similarly oxidised, yields an erythrite $C_{10}H_{16}(OH)_4$, m.p. 237°, which, under the action of dilute sulphuric acid, gives a mixture of thymol and carvacrol (C. 1909, II. 2159).

Terpinene Dihydro-halogenides.—These, like the corresponding dipentene compounds, occur in two stereo-isomeric forms, of which only the trans-form is solid at ordinary temperatures. They are formed from the terpinenes, but with greater ease, by the action of halogen hydride upon the bicyclic sabinene and thujene. Also from terpinene-terpin, and the terpineols, with glacial acetic halogen hydride. **trans-Terpinene dichloro-hydrate, dibromo-hydrate,** and **di-iodo-hydrate** melt at 52°, 59°, and 76°. A **terpinene monochloro-hydrate** $C_{10}H_{16}HCl$, bp.$_{12}$ 87°–92°, results from terpinene and sabinene with dry HCl in carbon bisulphide solution. It corresponds to terpineol-4, since sodium and alcohol reduce it to carvo-methene (B. **40**, 2959).

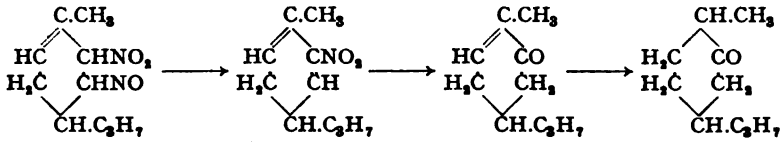
Phellandrene Group.—By α- and β-phellandrene we denote two isomeric dihydro-cymols, both marked by the ease with which they combine with nitrous acid to form well-marked pseudo-nitrosites. The phellandrenes belong to the most unstable terpenes, converted by acids into other terpenes, like dipentene and terpinene. With halogen hydride and bromine they only form liquid addition products, and, since they cannot be regenerated from the crystallised nitrites, they have not been hitherto obtained pure.

β-Phellandrene $C_{10}H_{16}=CH_2.C\begin{matrix}CH—CH_2\\ CH=CH\end{matrix}\!\!>\!CH.CH\!<\!\begin{matrix}CH_3\\ CH_3\end{matrix}$, bp. 173°–175°. is optically active and is pretty frequently found in ethereal oils, both with right-hand and left-hand rotation. d-α-Phellandrene has been found in water of fennel oil, elemi oil (A. **246**, 233), ginger-grass oil, while l-α-phellandrene has been found in Australian eucalyptus oil of *Eucalyptus amygdalina* and in aniseed oil (?). l-α-Phellandrene has been synthesised from the product of Δ^3-iso-propyl-cyclo-hexenone and CH_3MgI by rejection of water (A. **359**, 285), and also from chloro-phellandrene, the product of the action of PCl_5 upon carvotane-acetone, by reduction with sodium and alcohol (B. **38**, 1832).

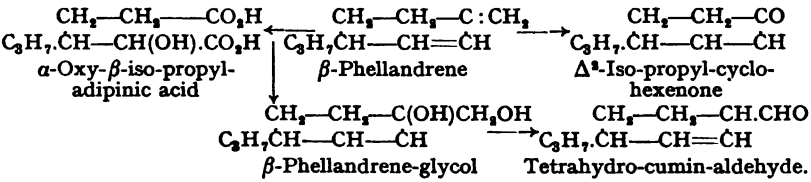
On oxidation with potassium permanganate, α-phellandrene produces α-oxy-β-iso-propyl-glutaric acid and iso-propyl-succinic acid. Sodium and alcohol reduce it to carvo-menthene (B. **86**, 1749).

The bimolecular **α-phellandrene nitrite,** obtained with nitrous acid, occurs in two stereo-isomeric (?) forms, m.p. 105° and 113°, and on reducing with zinc and glacial acetic acid it yields α-phellandrene-diamine $C_{10}H_{16}(NH_2)_2$, b.p. 133° (17 mm.), which shows that both

nitrogen atoms are linked with carbon. With bases, it does not yield nitrolamines like the formal nitrosites. With sodium alcoholate it splits off hypo-nitrous acid and forms **nitro-α-phellandrene,** b.p. 125°–129° (9 mm.), which can be reduced, with zinc and glacial acetic acid, to active *carvotane-acetone*, and, with sodium and alcohol, to *tetrahydro-carvone* (A. **336,** 9).



β-Phellandrene $CH_2=C\langle^{CH_2—CH_2}_{CH=CH}\rangle CH.CH\langle^{CH_2}_{CH_2}$, b.p.$_{11}$ 57°, occurs in a dextro-rotatory form in the oil of *Phellandrium aquaticum.* In the air it oxidises very readily, splits off the hemi-cyclic CH_2 group, and passes into Δ^2-iso-propyl-cyclo-hexenone (A. **343,** 29). By oxidation with a very dilute permanganate solution, we obtain a glycol $C_{10}H_{16}(OH)_2$, b.p. 150° (10 mm.), which, on treatment with dilute sulphuric acid, yields tetrahydro-cumin-aldehyde besides dihydro-cumin-alcohol. Stronger action by potassium permanganate produces α-oxy-β-iso-propyl-adipinic acid :



The **β-phellandrene nitrite** $C_9H_{14}(NC).CH_2.NO_2$, m.p. 98° and 102°, produced by nitrous acid, is reduced by zinc and glacial acetic acid to **β-phellandrene-diamine,** b.p. 134° (11 mm.), while sodium and alcohol reduce it to cumin-aldehyde. Sodium alcoholate converts it into **nitro-β-phellandrene** $C_{10}H_{15}NO_2$, which, on reduction with zinc and acetic acid, passes into dihydro-cumin-aldehyde (A. **340,** 1).

$\Delta^{2,4}$-Menthadiene $CH_3.CH\langle^{CH=CH}_{CH=CH}\rangle CH.CH(CH_3)_2$, b.p. 174°, usually obtained synthetically by V. Baeyer from succinylo-succinic ester by conversion into 1-methyl-4-iso-propyl-cyclo-hexandione-2,5, reduction, and rejection of $2H_2O$. It yields no crystalline bromide or nitrosite, and does not seem to be identical with any of the known terpenes (B. **26,** 232 ; **27,** 453).

$\Delta^{3,8(9)}$-p-Menthadiene $C_{10}H_{16}$, b.p. 184°, tetrahydro-p-toluylic acid ester with $MgICH_3$ (C. 1910, II. 80 ; see B. **39,** 2585).

Sylvestrene $C_{10}H_{16}=^{CH_3.C=CH—CH.C(CH_3):CH_2}_{\quad\quad\quad CH_2—CH_2—CH_2}$, b.p. 176°, has been found in the Indian, Swedish, and Russian turpentine oil, and oil of pine-needles. It is dextro-rotatory, $[\alpha]_D=+66{\cdot}32°$ (A. **252,** 149), and possesses a pleasant odour resembling lemons. Synthetically, it has been prepared from d-Δ^2-tetrahydro-m-toluic ester by trans-

position with CH_3MgI and elimination of water (Perkin). Its solution in acetic anhydride is coloured a deep blue by the addition of concentrated sulphuric acid. Similar behaviour is shown by carvestrene and dihydro-benzol, while other terpenes, under the same conditions, show a red or reddish-yellow colour. It is one of the most stable of terpenes, and cannot be transformed into isomeric terpenes by means of either heat or acids (A. **239**, 28). On bromination of its dihydrobromide and subsequent reduction with zinc dust and HCl, m-cymol is obtained, while limonene, treated similarly, gives p-cymol. Sylvestrene is probably, therefore, the limonene of the m-cymol series (B. **31**, 2067). Like limonene, it forms, by addition of two molecules halogen hydride, dihalogenides, which, however, in contrast with the corresponding limonene compounds, are optically active, and from which, by boiling with aniline and sodium acetate, optically active sylvestrene is regenerated. By treatment with dilute potash the dihydro-halogenides are converted into the alcohols corresponding to terpin and terpineol, viz. **sylveterpine** $C_{10}H_{18}(OH)_2$, m.p. 136°, and **sylveterpineole** $C_{10}H_{17}OH$, b.p. 210° (A. **357**, 72); **dihydro-chloride** $C_{10}H_{18}Cl_2$, m.p. 72°; **dihydro-bromide**, m.p. 72°; **dihydro-iodide**, m.p. 67°; **tetrabromide** $C_{10}H_{16}Br_4$, m.p. 135°; **nitroso-chloride** $C_{10}H_{16}(NO)Cl$, m.p. 107° (A. **252**, 150).

Carvestrene $C_{10}H_{16}$, boiling at 178°, results from the distillation of carylamine chlorohydrate. It is probably the optically inactive isomeride corresponding to sylvestrene (B. **27**, 3485). Since, like the latter, it passes into m-cymol, it is probably *the dipentene of the m-cymol series* (B. **31**, 1405). Blue coloration, see Sylvestrene. By nuclear synthesis it has been obtained from the racemic Δ^2-tetrahydro-m-toluic ester (C. 1907, I. 1408).

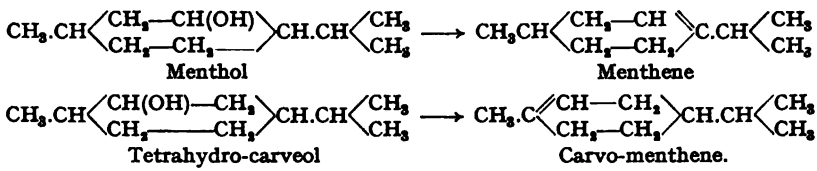
The *dihydro-chloride* melts at 52°, and the *dihydro-bromide* at 48°–50°. On the synthesis of a terpene linkage isomeric with carvestrene, viz. $\Delta^{6,8(9)}$-m-menthadiene, b.p. 177°, see C. 1909, I. 171.

Hydro-terpenes. — Hydrocarbons derived from menthol and tetrahydro-carveol as foundation substances, and containing two to four atoms more of hydrogen than the preceding bodies, bear close kinship to the latter. The two alcohols just mentioned are derived in such a manner from hexahydro-p-cymol that in both of them there are present secondary ring-alcohols of this hydrocarbon. When they lose water, menthene and carvo-menthene are produced. The production of the latter compounds from limonene and terpinene monochlorohydrate, as well as from α-phellandrene, by reduction with sodium and alcohol, has been mentioned above.

Carvo-menthene $C_{10}H_{18}$, b.p. 175° (cp. *J. pr. Ch.* 2, **66**, 274; B. **40**, 2959). Its nitroso-chloride melts at 87°, and its nitrol-benzyl-amine at 1007°.

Menthene, *mentho-menthene* $C_{10}H_{18}$, b.p. 167°, with specific gravity 0·806 or 0·814 (20°). It is best made by acting with potassium phenolate upon menthyl chloride (B. **29**, 1843); or by the dry distillation of *menthyl-xanthogenic methyl ester* $C_{10}H_{10}OCSSCH_3$ (B. **32**, 3332); it is obtained direct from menthol by heating with dilute sulphuric acid or oxalic acid (C. 1900, I. 1101; 1901, II. 1158; B. **37**, 1374). i-Menthene has been obtained from the condensation product of 1, 4-methyl-cyclo-hexanone with iso-propyl-magnesium iodide by splitting off water (C. 1906, I. 341). *Nitroso-chlorides*, see B. **29**, 4.

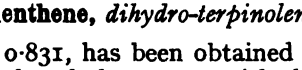
The constitution of the two hydrocarbons follows from their relation to carvacrol and menthol. Carvacrol readily results from a rearrangement of carvone, which, upon reduction, yields tetrahydrocarveol, with which menthol is isomeric. The constitution of menthol, on the other hand, is proved by conversion of the corresponding ketone, menthone, into 3-chloro-cymol and thymol. By removing water from these alcohols, or hydrogen chloride from their chlorides, two different tetrahydro-cymols are formed :

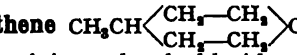


Menthol — Menthene

Tetrahydro-carveol — Carvo-menthene.

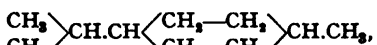
When oxidised with potassium permanganate, *menthene* yields (1) menthene glycol, (2) a keto-alcohol boiling at 105° (13·5 mm.), and (3) the fatty acids arising from menthone (B. **27,** 1636) ; while *carvo-menthene* yields (1) a *ketone aldehyde* $C_{10}H_{18}O_2$, b.p. about 120°, (2) a *ketonic acid* $C_{10}H_{18}O_3$, b.p.$_9$ about 175°, and (3) β-iso-propyl-glutaric acid (B. **40,** 2959).

A **$\Delta^{4(8)}$-menthene,** *dihydro-terpinolene*  , b.p. 173°, D 0·831, has been obtained from the condensation product of 1, 4-methyl-cyclo-hexanone with bromiso-butyric ester and zinc by rejection of water, and distillation of the resulting unsaturated acid. Nitroso-chloride, m.p. 102°. On boiling with dilute H_2SO_4 it transposes into i-mentho-menthene (A. **360,** 70). In the same manner the corresponding menthenes of the o- and m-series have been obtained (A. **360,** 75).

$\Delta^{8(9)}$-Menthene  , b.p.$_{14}$ 54°, is formed by reduction of iso-pulegol chloride with sodium and alcohol. On oxidation, it yields hexahydro-p-acetyl-toluol and hexahydro-p-toluic acid (B. **39,** 2582).

By reducing menthol with HI, or menthyl chloride with sodium and alcohol (B. **29,** 317 ; *J. pr. Ch.* 2, **60,** 158) a hydrocarbon has been obtained which is probably hexahydro-cymol.

Hexahydro-cymol, *menthane, mentho-naphthene*

 ,

b.p. 169°, D_0 0·8066. The same hydrocarbon is probably represented by the hexahydro-cymol obtained by the reduction of terpin hydrate (B. **28,** R. 433), terpineol (C. 1905, II. 135), and d-limonene (C. 1910, I. 349), as well as resin oil.

2. Alcohols of the Monocyclic Terpene or Menthane Group.

Monacid Menthane Alcohols.—Hexahydro-p-cymol yields the isomeric menthols.

Secondary Menthols.—l-Menthol, mentha-camphor, 5-methyl-2-

iso-propyl-hexahydro-phenol $CH_3.CH\langle^{CH_2.CH(OH)}_{CH_2.CH_2}\rangle CH.CH(CH_3)_2$ (see above), m.p. 44° and b.p. 212°. It is the chief constituent of peppermint oil (from *Mentha piperita* and *Mentha arvensis*, var. *piperascens*). It is formed in the reduction of menthone (*J. pr. Ch.* 2, **55**, 14), and is oxidised by chromic acid to l-menthone. By the exit of water it yields menthene (see above), and by reduction hexahydrocymol results (above). Potassium permanganate converts it into **oxomenthylic acid** $CH_3.CH\langle^{CH_2.CO_2H}_{CH_2.CH_2}\rangle CO.CH.(CH_3)_2$, boiling at 174° (15 mm.) (A. **289**, 362), and **β-methyl-adipic acid** $CH_3.CH\langle^{CH_2.CO_2H}_{CH_2.CH_2}\rangle CO_2H$, melting at 89° (B. **27**, 1818).

A mixture of two racemic menthols, m.p. 25° and 49°, is obtained by the reduction of thymol with hydrogen and nickel. From the first of these, by splitting up the corresponding phthalic ester acid with cinchonin or brucin, we obtain the natural l-menthol (C. 1909, I. 1872).

Menthyl chloride $C_{10}H_{19}Cl$ boils at 204°. The **ethyl ether** boils at 212°, and the **benzoyl ester** melts at 54°. **Menthyl-xanthogenic methyl ester,** m.p. 39°, gives menthene on dry distillation (B. **35**, 2473). **Isovalerianic ester,** b.p.$_{10}$ 126°, is recommended under the name of "*validol*" as a remedy for sea-sickness. The chloro-methyl-menthyl ether, formed by the action of HCl upon a mixture of menthol and formaldehyde, is used under the name "*formane*" as an antiseptic. Its composition is $C_{10}H_{19}OCH_2Cl$, b.p.$_{16}$ 161°.

Tetrahydro-carveol, *carvo-menthol* $CH_3.CH\langle^{CH(OH)-CH_2}_{CH_2-\!-\!-CH_2}\rangle CH.CH(CH_3)_2$, isomeric with menthol, is a thick oil, volatile without decomposition. It is formed when tetrahydro-carvone and carvenone are reduced in moist ethereal solution with metallic sodium. A mixture of racemic carvo-menthols is obtained by the reduction of carvacrol with Ni and H (C. 1908, I. 733).

Its genetic connection with carvacrol (see above) would indicate its constitution.

Tertiary menthols are produced when their hydro-iodic acid esters, addition products of HI and menthene by means of carvo-menthene, are treated with moist silver oxide (see also B. **29**, 1844; *J. pr. Ch.* 2, **60**, 259). It is noteworthy that the addition of the halogen hydrides to the menthenes produces the same tertiary menthyl halogenides as are obtained from menthol and tetrahydro-carveol, with the phosphorous halogenides and halogen hydrides.

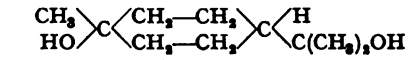
Tertiary menthol-4 $CH_3.CH\langle^{CH_2-\!-\!-CH_2}_{CH_2-\!-\!-CH_2}\rangle C(OH).CH(CH_3)_2$, b.p. 100° (20 mm.), has a faint peppermint-like odour. It is formed by the action of iso-propyl-magnesium iodide upon 1, 4-methyl-cyclohexanone (C. 1906, II. 342). On heating with KHSO it yields **$\Delta^{4(8)}$-menthene.**

Tertiary carvo-menthol $CH_3C(OH)\langle^{CH_2-\!-\!-CH_2}_{CH_2-\!-\!-CH_2}\rangle CH.CH(CH_3)_2$ boils at 96°–100° (17 mm.).

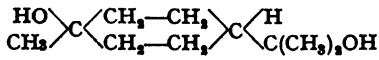
Tertiary menthanol-8 $CH_3CH\langle^{CH_2-\!-\!-CH_2}_{CH_2-\!-\!-CH_2}\rangle CH.C(OH)(CH_3)_2$, m.p. 36°,

b.p. 207°, from hexahydro-p-toluic ester and methyl-magnesium iodide (C. 1905, II. 239).

Diacid Alcohols.—In this group are the two terpins, cis-terpin and trans-terpin, corresponding to the cis- and trans-dipentene-dihydro-halogenides, with which they are intimately related. At present the following formulæ are assigned them (see B. **29,** 5; C. 1897, II. 420):



cis-Terpin



trans-Terpin.

These are in harmony with the oxidation of terpin hydrate to terebic acid, as well as with its formation from linalool. Cineol is to be regarded as the oxide corresponding to the cis-terpin.

Terpin, *cis-terpin* $C_{10}H_{18}(OH)_2$, melting at 104° and boiling at 258°, readily attracts water and passes into a body distinguished by its great power of crystallisation, viz.:

Terpin hydrate $C_{10}H_{18}(OH)_2+H_2O$, m.p. 117°, from which it is prepared by protracted heating to 100°. Terpin corresponds to cis-dipentene-dihydro-bromide, from which it can be obtained by treatment with silver acetate in glacial acetic acid, and saponifying the resulting diacetyl derivative with alcoholic potash. Terpin hydrate is also produced if turpentine oil is allowed to stand with dilute nitric acid and alcohol (A. **227,** 284), as well as from pinene, dipentene, and d-limonene with dilute acids. It forms, furthermore, on bringing dipentene and d-limonene dihydro-chloride into contact with water, and when terpineol and cineol are acted upon by dilute acids. Synthetically, it has been obtained by the action of methyl-magnesium iodide upon 1, 4-cyclo-hexanone-carboxylic ester (C. 1907, I. 1412).

The haloid acids convert terpin hydrate into the cis- and trans-dihydro-halides of dipentene. When boiled with dilute acids it passes into terpineols (B. **27,** 443, 815), cineol, dipentene, terpins, and terpinolenes.

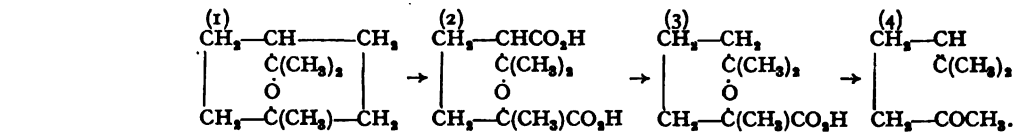
trans-Terpin $C_{10}H_{18}(OH)_2$, m.p. 156°–158° and b.p. 263°–265°, is formed from trans-dipentene-dihydro-bromide (see cis-Terpin), into which it finally reverts upon treatment with hydrogen bromide. It does not combine with water of crystallisation.

Cineol, *eucalyptol* $C_{10}H_{18}O$, b.p. 176°, with specific gravity 0·923 (16°), $n_D=1·4559$, is a liquid with a camphor-like odour, and represents the glycol anhydride corresponding to cis-terpin.

It occurs in many ethereal oils, in *oleum cinæ*, the worm-seed oil of *Artemisia cina*, cajeput oil, eucalyptus oil, rosemary oil, sage oil, etc. Hydrochloric acid gas conducted into a petroleum ether solution of cineol precipitates an unstable addition product $C_{10}H_{18}O.HCl$ (?), which water resolves into its components, and which serves for the separation of cineol. With phosphoric acid, resorcin, hydrogen ferro- and ferri-cyanide, etc., cineol forms compounds resembling salts (B. **34,** 2689; C. 1907, II. 240).

In glacial acetic acid solution the haloid acids change cineol into dipentene dihydro-halides. At low temperatures hydrogen bromide produces cis-dipentene-dihydro-bromide. P_2S_5 converts cineol into cymol. Potassium permanganate oxidises cineol (1) into cineolic acid

(2), the anhydride (3) of which yields, upon distillation, methyl-hexylene ketone or methyl-heptenone (4), while the latter may be arranged to m-dihydro-isoxylene (5). This series of reactions is shown in the following diagram :



Cineolic acid melts at 196°–197° with decomposition; its anhydride melts at 78° and boils at 157° (13 mm.). On heating with concentrated H_2SO_4 it yields 1, 3-dimethyl-benzoic acid (B. **89**, 4083). **Cinenic acid** $C_9H_{16}O_3$, m.p. 84°, is formed synthetically from the hydrate of methyl-heptenone by addition of prussic acid and saponification. By the action of concentrated H_2SO_4 it passes into δ-acetyl-*aa*-dimethyl-valerianic acid with migration of a methyl group (B. **33**, 1129; **34**, 2191; **41**, 1278).

As terpin corresponds to the dipentene-dihalogenides, so we have, corresponding to the terpinene dihalogenides, **terpinene-terpin** $CH_3(OH)C\langle\begin{matrix}CH_2—CH_2\\CH_2—CH_2\end{matrix}\rangle C(OH).CH(CH_3)_2$, m.p. 138°, b.p. 250°, which sublimes on heating. It is formed by the action of dilute potash upon terpinene dichlorohydrate, to which it reverts on treating with glacial acetic-hydrochloric acid. It is also obtained from sabinene, thujene, and terpinenols with dilute sulphuric acid (A. **356**, 200). On heating with oxalic acid it splits off water and passes into terpinenol-4 and **1, 4-cineol**, *terpinene-cineol* $CH_3C\langle\begin{matrix}CH_2—CH_2\\O\\CH_2—CH_2\end{matrix}\rangle C.CH(CH_3)_2$, b.p. 173°. This, with HBr, yields terpinene dibromo-hydrate (A. **356**, 204).

On the meta-series compound corresponding to terpin, *sylveterpin*, see above, and C. 1907, I. 1408.

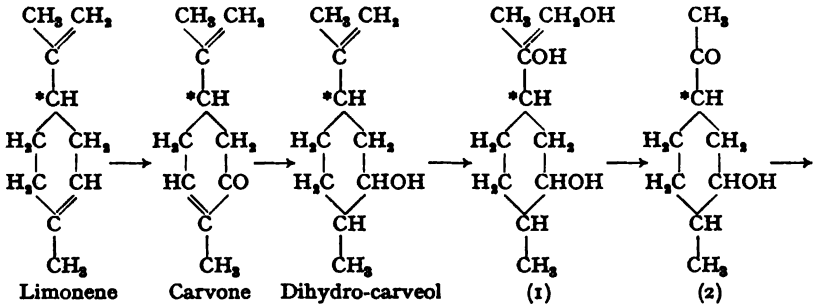
Menthene-glycol $C_{10}H_{18}(OH)_2$, melting at 77° and boiling at 130° (13 mm.), results when menthene is oxidised with potassium permanganate (B. **27**, 1636). An isomeric 3, 8-menthene-glycol $C_{10}H_{18}(OH)_2$, m.p. 81°, b.p.$_{10}$ 145°, is obtained besides iso-pulegol by treating citronellal with dilute H_2SO_4; on withdrawing water it passes into iso-pulegol (C. 1897, II. 304).

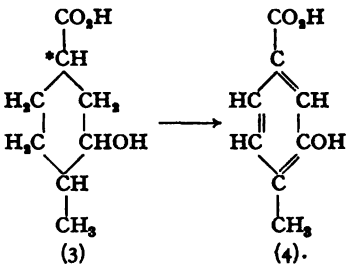
2, 8-Dioxy-hexahydro-cymol $C_{10}H_{18}[2, 8](OH)_2$, α-form m.p. 113°, β-form m.p. 103°, is formed by reduction of oxy-dihydro-carvone, or by shaking up dihydro-carveol with dilute H_2SO_4. On boiling with 25 per cent. H_2SO_4, it yields an oxide isomeric with cineol, dihydro-pinol $C_{10}H_{18}O$, b.p.$_9$ 58°, which unites with potassium ferricyanide to a crystalline compound (B. **88**, 1719).

(*c*) **Triacid menthane alcohols** have been obtained by oxidising menthene alcohols with potassium permanganate.

1. **2, 8, 9-Trioxy-hexahydro-cymol** $C_{10}H_{17}[2, 8, 9](OH)_3$ (1), from dihydro-carveol (see below), is a syrup, and with dilute sulphuric acid yields an indifferent oxide $C_{10}H_{16}O$, boiling at 196°–199° (A. **277**, 152); while upon oxidation with chromic acid it forms a ketone-alcohol, **5-acetyl-hexahydro-o-cresol**, melting at 58° (2), which, upon further

oxidation, changes to **hexahydro-m-oxy-p-toluic acid**, melting at 153° (3). The constitution of this last acid is evident from its conversion by bromine into **m-oxy-p-toluic acid**, melting at 203° (4). These experiments give rise to the constitution formulæ (B. **28**, 2141) :





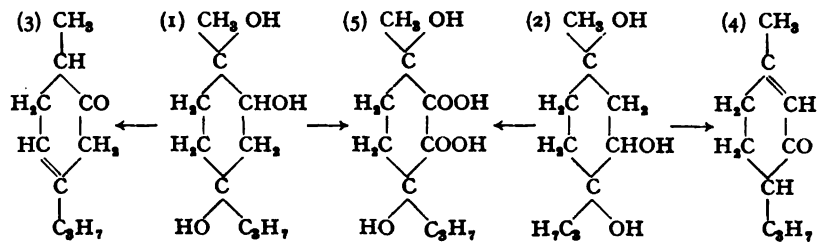
2. **1, 2, 8-Trioxy-hexahydro-cymol, dioxy-terpineol** $C_{10}H_{17}(OH)_3$, melting at 122°, formed from the terpineol melting at 35°, passes into carvenone when it is acted upon with dilute sulphuric acid (A. **277**, 122).

3. **1, 8, 9-Trioxy-hexahydro-cymol** $C_{10}H_{17}[1, 8, 9](OH)_3$, m.p. 118°, from β-terpineol.

4. **1, 4, 8-Trioxy-hexahydro-cymol** $C_{10}H_{17}[1, 4, 8](OH)_3+3H_2O$, melts in the anhydrous state at 110°–112° and boils at 200° (20 mm.). It is formed from $\Delta^{4,8}$-terpineol (B. **28**, 2296).

5. **1, 2, 4-Trioxy-hexahydro-cymol** (1) $C_{10}H_{17}[1, 2, 4](OH)_3+H_2O$, m.p. 117°, anhydrous, m.p. 129°, and

6. **1, 3, 4-Trioxy-hexahydro-cymol** (2) $C_{10}H_{17}[1, 3, 4](OH)_3$, m.p. 121°, are formed by the oxidation of terpinenol-4 and terpinenol-1. On heating with HCl the former passes into carvenone (3) and the latter into Δ^1-menthenone (4). $KMnO_4$ oxidises both to $\alpha\alpha_1$-dioxy-α-methyl-α_1-iso-propyl-adipinic acid (5). These transformations, important for the constitution of terpinenols and terpinene-terpin, are shown in the following scheme (A. **356**, 207 ; **362**, 261) :

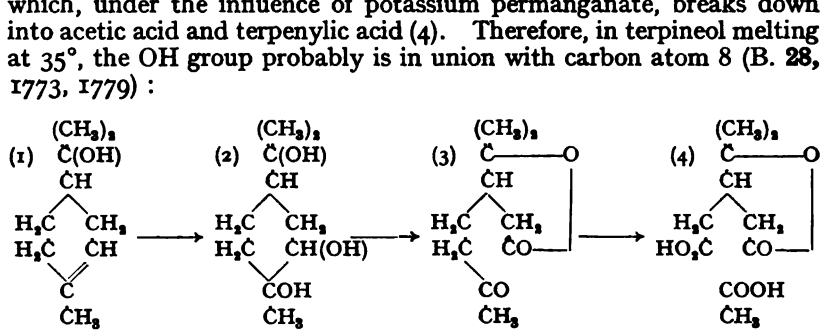


Tetra-acid-methane alcohols are formed by the oxidation of some terpenes with potassium permanganate: (1) Limonetrite $C_{10}H_{16}(OH)_4$, m.p. 192°, from d-limonene (B. **23**, 2315; **28**, 2149); (2) erythrite of terpinolene, m.p. 150° (anhydrous) (A. **368**, 10); (3) erythrite from γ-terpinene, m.p. 237°, gives a mixture of carvacrol and thymol on heating with dilute H_2SO_4 (A. **362**, 298; C. 1909, II. 2159).

II. **Menthene Alcohols** $C_{10}H_{17}$.—On oxidation with potassium permanganate these give three-acid alcohols (see above).

Terpineols.—The "*liquid terpineol*" used in perfumery, obtained from terpin hydrate by elimination of $2H_2O$ with dilute H_2SO_4, consists chiefly of the two isomeric α- and β-terpineols, m.p. 35° and 32°:

α-Terpineol, Δ^1-*menthenol*-8 $CH_3.C\begin{matrix}CH—CH_2\\ CH_2—CH_2\end{matrix}\!\!>\!CH.C(OH)(CH_3)_2$, m.p. (optically inactive form) 35°, (active forms) 37°–38°, b.p. 219°, D_{15} 0·939, can also be obtained from linalool and geraniol. By nuclear synthesis it is obtained through the action of methyl-magnesium iodide upon Δ^1-tetrahydro-p-toluic ester (C. 1909, I. 170). Terpineols, of various origins, may be either active or inactive optically (B. **28**, 2180). A specially strongly lævo-rotatory α-terpineol, $\alpha_D = -106°$, is obtained by the action of dilute H_2SO_4 upon methyl-nopinol (A. **360**, 88). On a lævo-rotatory terpineol from oil of turpentine, see C. 1889, I. 1241. Terpineol combines very readily with nitrosyl chloride. When hydrogen chloride is withdrawn from this body, an *oxy-oxime*, melting at 134°, is produced. Boiling dilute acids change it to carvacrol and carvone (B. **29**, R. 587). Hence it follows that in terpineol and carvone the carbon atoms are similarly grouped. Terpineol nitroso-chloride and limonene nitroso-chloride are correspondingly constituted (B. **29**, 9). Potassium permanganate oxidises terpineol (1) into trioxy-hexahydro-cymene, melting at 121° (2), while with chromic acid it yields a ketone-lactone, homo-terpenylic acid methyl-ketone $C_{10}H_{16}O_3$ (3), which, under the influence of potassium permanganate, breaks down into acetic acid and terpenylic acid (4). Therefore, in terpineol melting at 35°, the OH group probably is in union with carbon atom 8 (B. **28**, 1773, 1779):



When terpineol is heated with potassium bisulphate it changes to *dipentene*, and when boiled with oxalic acid to *terpinolene* (A. **275**, 104; **368**, 10).

β-Terpineol, $\Delta^{8(9)}$-*menthenol*-1 $CH_3C(OH)\begin{matrix}CH_2—CH_2\\ CH_2—CH_2\end{matrix}\!\!>\!CH.C\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>$, m.p. 32°, b.p. 210°, D_{15} 0·923; nitroso-chloride, m.p. 103° (A. **345**, 127), yields with permanganate 1, 8, 9-trioxy-hexahydro-cymol, which on further oxidation with chromic acid yields 4-acetyl-1, 1-methyl-cyclo-hexanol; the latter may be converted into tetrahydro-p-acetyl-

toluol, p-acetyl-toluol, and p-toluic acid (B. **35,** 2147; A. **324,** 79). For synthesis of β-terpineol, see C. 1904, II. 330.

γ-Terpineol, $\Delta^{4(8)}$-*menthenol*-1 $CH_3.C(OH)\langle^{CH_2—CH_2}_{CH_2—CH_2}\rangle C=C\langle^{CH_3}_{CH_3}$, melts at 69°. Its acetate results on treating tribromo-terpane or tetrahydro-dipentene tribromide with glacial acetic acid and zinc dust. Glacial acetic acid and HCl convert it into a mixture of dipentene and terpinene dichlorohydrate (A. **350,** 160). With NOCl it forms a *blue* nitroso-chloride, just as tetramethyl-ethylene does. Consequently it probably also contains a tertiary-tertiary double union. In addition, its OH group must be in such a position that dipentene dihydrobromide can be produced with hydrogen bromide.

Terpinenols.—As from terpin, so also from terpinene-terpin, unsaturated alcohols may be obtained, by splitting off one molecule of water. These are termed terpinenols (A. **356,** 206; **362,** 261).

Terpinenol-4, Δ^1-*menthenol*-4 $CH_3C\langle^{CH—CH_2}_{CH_2—CH_2}\rangle C(OH).CH\langle^{CH_3}_{CH_3}$, b.p. 212°, found in dextro-form in cardamomene and majoran oil (A. **356,** 168). d-Terpineol-4 is formed by shaking up sabinene and thujene in dilute H_2SO_4, sabinene hydrate being formed intermediately, and easily passing into terpinenol-4. l-Terpinenol-4 is produced by the action of dilute potash upon terpinene dihydro-chloride, and from terpinene-terpin with aqueous oxalic acid. With glacial acetic hydrogen haloids it yields terpinene dihaloids, with dilute H_2SO_4 terpinene-terpin. By oxidation with MnO_4K we obtain the 1, 2, 4-trioxy-hexahydro-cymol.

Terpinenol-1, Δ^3-*menthenol*-1 $CH_3.C(OH)\langle^{CH_2—CH}_{CH_2—CH_2}\rangle C.CH\langle^{CH_3}_{CH_3}$, b.p. 209°, is found in the first samples of industrial terpineol. It is synthesised from Δ^3-iso-propyl-cyclo-hexanone with methyl-magnesium iodide. On oxidation it yields 1, 3, 4- trioxy-hexahydro-cymol.

Dihydro-carveol, $\Delta^{8(9)}$-*menthenol*-2 $CH_3CH\langle^{CH(OH)—CH_2}_{CH_2——CH_2}\rangle CH.C\langle^{CH_3}_{CH_3}$, b.p. 224°, D_{15} 0·937, n_D=1·482, optically active, with a pleasant odour recalling terpineols, was found in carraway oil (C. 1905, I. 1470); it is formed by the reduction of carvone; dihydro-carveol-xanthogenic methyl ester on dry distillation yields d-limonene (C. 1908, I. 1180).

Iso-pulegol, $\Delta^{8(9)}$-*menthenol*-3 $CH_3.CH\langle^{CH_2.CH(OH)}_{CH_2——CH_2}\rangle CH.C\langle^{CH_3}_{CH_2}$, b.p.$_{13}$ 91°, from the isomerisation of citronellal with acids. On oxidation it passes into the ketone, iso-pulegone.

Δ^3-**Menthenol-8** $CH_3CH\langle^{CH_2—CH}_{CH_2—CH_2}\rangle C.C(OH)\langle^{CH_3}_{CH_3}$, m.p. 39°, b.p.$_{14}$ 97°, by the action of CH_3MgI upon Δ^3-tetrahydro-p-toluic ester or Δ^3-tetrahydro-p-acetyl-toluol (C. 1910, II. 80).

Δ^2-**Menthenol-1** $CH_3(OH)C\langle^{CH=CH}_{CH_2—CH_2}\rangle CH.CH\langle^{CH_3}_{CH_3}$, b.p.$_{10}$ 92°, by transposition of Δ^2-iso-propyl-cyclo-hexenone-4 with CH_3MgI. Easily loses water and forms α-phellandrene (A. **359,** 283).

Menthadiene Alcohols.—Carveol-methyl ether $C_{10}H_{15}OCH_3$, boiling at 208°–212°, with sp. gr. 0·9065, n_D=1·47586 (18°), represents the methyl ether of such an alcohol. It is formed in the action of

sodium upon the alcoholic solution of limonene tetrabromide. Chromic acid oxidises it to inactive carvone (A. **281**, 140).

3. Bases of the Monocyclic Terpene or Menthane Group.

Menthane bases have been obtained by the reduction of the oximes of the methane-ketones with sodium and alcohol, or upon heating the ketones with ammonium formate.

d-Menthylamine and **l-menthylamine** $CH_3.CH\langle\begin{matrix}CH_2-CH\\CH_2-CH_2\end{matrix}\rangle\begin{matrix}C(NH_2)\\CH\end{matrix}.CH(CH_3)_2$, boiling at 205°, have an unpleasant odour, and attract CO_2 from the air. The bases have opposite, but *unequal*, rotatory power; the same is true of their derivatives (A. **276**, 299). They can be separated by means of their formyl compounds, both of which are formed on heating menthene with ammonium formate. **d-Formyl-menthylamine**, melting at 117°, dissolves with more difficulty. **l-Formyl-menthylamine** melts at 102°. l-Menthylamine can also be obtained from l-menthoxime. With HNO_2, l-menthylamine passes straight into l-menthol, while d-menthylamine mostly forms menthene (conclusions as to configuration, see A. **300**, 278; **353**, 323). On treating the bromyl compounds of menthylamines with Ag_2O, l-menthylamine yields **l-menthyl-hydrazin** $C_{10}H_{19}NHNH_2$, b.p. 241°, while d-menthylamine forms **menthazin** $C_{10}H_{18}:N.N:C_{10}H_{18}$, m.p. 51° (C. 1900, I. 654). *l-Menthyl-hydrazin is useful for splitting up racemic aldehydes and ketones* (B. **36**, 1192). l-Menthyl-carbimide $C_{10}H_{19}.N:CO$, b.p.$_{12}$ 110°, from l-menthylamine, chloro-carbonic ester, and distillation of the resulting menthyl-carbaminic ester with P_2O_5. May be used for splitting up racemic alcohols (C. 1904, II. 332).

Tetrahydro-carvylamine, *carvo-menthylamine*

$$CH_3.CH\langle\begin{matrix}CH(NH_2)-CH_2\\CH_2-CH_2\end{matrix}\rangle CH.CH(CH_3)_2$$

boils at 212° (A. **277**, 137; C. 1908, I. 733).

Tert. menthylamine $CH_3.CH\langle\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}\rangle C(NH_2)CH(CH_3)_2$ and **tert. carvo-menthylamine** $.CH_3(NH_2)C\langle\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}\rangle CH.CH(CH_3)_2$ have been obtained by the interaction of menthene hydrobromide, carvo-menthene hydrobromide, and silver cyanate, with subsequent saponification (B. **26**, 2270, 2562).

2, 4-Diamido-menthane $C_{10}H_{18}(NH_2)_2$, b.p.$_{12}$ 121°, from carvenone-oxamine oxime (B. **41**, 2528).

Menthene bases have been prepared by the reduction of the oximes of menthene-ketones. **Carvenylamine** $C_{10}H_{17}NH_2$, b.p.$_{10}$ 86°–89°, from carvenone oxime with Al amalgam. Its chlorohydrate yields α-terpinene on distillation (B. **41**, 2524).

Dihydro-carvylamine $C_{10}H_{17}NH_2$, b.p. 219°, with sp. gr. 0·889 (20°), $n_D=1·48294$, is optically active, and is obtained from carvonoxime $C_{10}H_{14}:NOH$. Its chlorohydrate breaks down completely at 200° into cymol and terpinene, with migration of linkage (A. **368**, 13).

Pulegonamine (A. **262**, 13; B. **29**, R. 173).

Nitrolamines have been obtained from nitroso-chlorides—*e.g.* limonene—by transposition with primary and secondary bases.

4. The Ring-ketones of the Monocyclic Terpene or Menthane Group.

Ketones like these are found in the vegetable kingdom. They are produced by the oxidation of the corresponding secondary alcohols, and by continued oxidation they change to cyclic and aliphatic carboxylic acids—decomposition products,—the constitution of which furnishes insight into the constitution of the ring-ketones and their derivatives. The ring-ketones of the terpane group, like other ketones, are characterised by their oximes and the sparing solubility of their semi-carbazones.

(*a*) **Keto-menthanes, keto-hexahydro-p-cymols** $C_{10}H_{18}O$.

Menthone $CH_3.CH\langle^{CH_2.CO}_{CH_2.CH_2}\rangle CH.CH(CH_3)_2$, boiling at 208°, sustains the same relation to menthol that camphor bears to borneol. It occurs in Japanese, American, and Russian peppermint oils, together with menthol, esters of menthol, menthene, and limonene. Menthone is known in two optically active modifications. l-Menthone is obtained upon oxidising menthol with potassium bichromate and sulphuric acid at a temperature not exceeding 50° (A. **250,** 322). Its specific gravity equals 0·896 (20°), $[\alpha]_D = -28°$. Concentrated sulphuric acid, in the cold, rearranges l-menthone to d-menthone, $[\alpha]_D = +93·2°$ (B. **42,** 846).

A d-menthone, $[\alpha]_D = +43°\ 66'$, is found in the American polei oil from *Hedeoma pulegioides* (C. 1907, II. 242). Synthetically, i-menthone has been formed from β-methyl-pimelinic ester by cyclic aceto-acetic ester condensation, introduction of the iso-propyl group, and saponification (B. **34,** 3793).

An optically active menthone is formed from the active 1, 3-methyl-cyclo-hexanone obtained by breaking up pulegone, by treating with sodium amide and iso-propyl iodide (C. 1905, I. 605); for other syntheses of menthone, see A. **342,** 306; **357,** 209; also Rhodinal.

The constitution of menthone is demonstrated (1) by its conversion into 3-chloro-cymol; PCl_5 changes menthone to *dichloro-hexahydro-cymol*, which splits off hydrogen chloride and becomes *tetrahydro-chloro-cymol*; this in turn, by the action of bromine and quinolin, loses hydrogen, and 3-*chloro-cymol* results (B. **29,** 314). (2) By the formation of *thymol* through the elimination of 2HBr from **dibromo-menthone** $C_{10}H_{16}Br_2O$, melting at 80°, which is produced in the bromination of menthone in chloroform solution (B. **29,** 418).

When l-menthone is reduced by sodium it forms *l-menthol*, while with ammonium formate the product is L-menthylamine. Potassium permanganate oxidises it to *oxo-menthylic acid* $CH_3.CH\langle^{CH_2.CO_2H}_{CH_2.CH_2}\rangle CO.CH(CH_3)_2$, and *β-methyl-adipic acid* (B. **27,** 1820).

Caro's acid produces the ε-lactone of *dimethyl-octanolic acid* $CH_3CH\langle^{CH_2—CO—O}_{CH_2—CH_2—CH.CH(CH_3)_2}$ (B. **27,** 1820; **32,** 3621; **33,** 860); dilute nitric acid produces nitro-menthone, which can be reduced to amido-menthone (C. 1898, II. 301).

Amyl nitrite and hydrochloric acid convert menthone into nitroso-menthone and **menthoximic acid,** melting at 98°. This is the oxime of oxo-menthylic acid (B. **29,** 27).

Illumination of an aqueous alcoholic solution of menthone leads

to the splitting of the ring and produces *decylic acid* $(CH_3)_2CH.(CH_2)_3CH(CH_3)CH_2COOH$, and an aldehyde $C_{10}H_{18}O$, possibly identical with a mentho-citronellal obtained by a transformation of menthone-oxime (B. **40**, 2419)

Sodium and amyl formate change menthone to **oxy-methylene-menthone,** boiling at 121° (12 mm.).

Benzylidene-menthone, m.p. 51°, b.p.$_{12}$ 189°, gives, on reduction **benzyl-menthone,** b.p.$_{10}$ 175°–178° (B. **37**, 232). With sodium and CO_2, in ether solution, menthone gives **menthone-mono-** and **dicarboxylic acids** (C. 1897, II. 759).

l-Menthone-oxime, m.p. 61°, b.p. 250°, $[\alpha]_D = -42°$, is transposed into l-menthone-isoxime by PCl_5 in chloroform, or by acetic anhydride, or by concentrated H_2SO_4. The substance formed is the ϵ-lactame of an ϵ-amido-methyl-iso-propyl-capronic acid, m.p. 119°, b.p. 295°, $[\alpha]_D = -52{\cdot}25°$. With P_2O_5 both bodies yield **mentho-nitrile** $C_9H_{17}CN$, b.p. 225°, which, on saponification, passes into the liquid **menthonenic acid** $C_9H_{17}COOH$; the latter is constituted somewhat like citronellic acid, but is not identical. The menthonylamine produced by the reduction of mentho-nitrile yields with HNO_2 a mentho-citronellol closely related to citronellol (A. **296**, 120).

Tetrahydro-carvone $CH_3.CH\langle\begin{matrix}CO.CH_2\\CH_2.CH_2\end{matrix}\rangle CH.CH(CH_3)_2$, with sp. gr. 0·904 (20°), $n_D = 1{\cdot}45539$, is produced in the oxidation of tetrahydro-carveol and by reduction of carone with Na in moist ether. Benzylidene compound, m.p. 175° (A. **305**, 266). The *oxime* melts at 104°, the *α-isoxime* at 51°. *β-Isoxime* melts at 104°. The *semi-carbazone* melts at 174° (A. **277**, 133; **286**, 107; B. **26**, 822). When oxidised with potassium permanganate or treated with amyl nitrite and hydrochloric acid, tetrahydro-carvone is decomposed like menthone with the production of an acid, $CH_3.CO\langle\begin{matrix}HOOC—CH_2\\CH_2—CH_2\end{matrix}\rangle CH.C_3H_7$, *β-iso-propyl-δ-acetyl-valeric acid*, isomeric with oxo-menthylic acid. Energetic oxidation produces iso-propyl-succinic acid (B. **29**, 27).

With Caro's acid we obtain the ϵ-lactone of *iso-propyl-heptanolic acid* $\begin{matrix}O——CO—CH_2\\CH_3CH—CH_2—CH_2\end{matrix}\rangle CHC_3H_7$ (B. **32**, 3629).

(*b*) **Keto-menthenes** $C_{10}H_{16}O$ occur to a certain extent in nature, others are produced by the oxidation of the corresponding alcohols. They contain *one double* union.

Δ^3-Methene-5-ketone $CH_3CH\langle\begin{matrix}CH_2—CH\\CH_2—CO\end{matrix}\rangle CC_3H_7$, b.p. 213°, D_{20} 0·918, $n_D = 1{\cdot}4720$; its oxime, *nitroso-menthene*, is obtained from **menthene nitroso-chloride** by splitting off HCl (A. **305**, 272; **362**, 275).

Δ^1-Menthene-3-ketone $CH_3C\langle\begin{matrix}CH——CO\\CH_2—CH_2\end{matrix}\rangle CHC_3H_7$, b.p. 236°, semi-carbazone, m.p. 225°, has been found in Japanese peppermint oil; it is formed besides cymol on heating 1, 3, 4-trioxy-hexahydro-cymol with HCl (A. **362**, 271).

Dihydro-carvone, $\Delta^{8(9)}$-*menthene-2-on* $CH_3CH\langle\begin{matrix}CH_2—CH_2\\CO—CH_2\end{matrix}\rangle CH.C\langle\begin{matrix}CH_2\\CH_2\end{matrix}$, b.p. 221°, D_{19} 0·928, $n_D = 1{\cdot}47174$, was found in carraway oil (C. 1905, I. 1470); the d- and l-forms are produced from the corresponding dihydro-carveols by oxidation, or direct by the reduction of the carvones

with zinc dust and alcoholic potash (A. **279**, 377). Benzylidene compound, b.p.$_{10}$ 187°–190° (A. **305**, 268).

The *oximes* melt at 88°, and unite to the inactive [*d*+*l*]-*oxime*, melting at 115°. Boiling ferric chloride converts dihydro-carvone into carvacrol; cp. carvenone and carone. Oxidation with potassium permanganate and afterwards with chromic acid changes it to 2, 5-*methyl-acetyl-cyclo-hexanone* (B. **28**, 2147, 2704). On the decomposition of dihydro-carvone by light, see B. **41**, 1928.

Carvenone, *carveol*, Δ^{3}-*menthene-2-on* $CH_3CH\langle^{CO\text{—}CH}_{CH_2\text{—}CH_2}\rangle C.CH\langle^{CH_3}_{CH_3}$, b.p. 232°, D 0·927, n_D'=1·4822, results from 1, 2, 8- and 1, 2, 4-trioxy-hexahydro-cymol on heating with dilute sulphuric acid besides cymol; by isomerising dihydro-carvone and carone with mineral or formic acids; by treating camphor, or rather dichloro-camphane, with H_2SO_4; and by reduction of α-terpinene nitrosite with zinc and glacial acetic acid (*J. pr. Ch.* 2, **60**, 261; A. **314**, 369). Oxime, m.p. 91°. Hydroxylamino-oxime, m.p. 163° (B. **31**, 2896). Semi-carbazone, m.p. 202°. It is closely related to carvotan-acetone. Boiling ferric chloride oxidises carvenone to carvacrol, while heating with P anhydride produces cymol, and permanganate α-methyl-glutaric acid (A. **314**, 380). With PCl_5 it produces **monochloro-carvenone** $C_{10}H_{15}Cl$, b.p.$_{10}$ 95°–98°, which on reduction with Na and alcohol yields α-terpinene (B. **41**, 4477).

Carvotan-acetone, Δ^{1}-*menthene-6-on* $CH_3C\langle^{CH\text{—}CH_2}_{CO\text{—}CH_2}\rangle CH.CH\langle^{CH_3}_{CH_3}$, b.p. 228°, D_{21} 0·938, n_D=1·47926, results in an inactive form from the heating of thujone (tanacetone) to 280°. Its oxime melts at 92°, and its semi-carbazone at 177° (B. **28**, 1959). Optically active dextro- and lævo-rotatory carvotan-acetone, $[\alpha]_D$+19·2°, is obtained by careful reduction of α-phellandrene nitrite (A. **336**, 39). Its oxime melts at 72°, its semi-carbazone at 173°. A dextro-rotatory carvotan-acetone has also been obtained from carvone hydrobromide by reduction with zinc dust and methyl alcohol (B. **34**, 1924). With H_2S it combines like carvone to form the compound $(C_{10}H_{16}O)_2H_2S$, m.p. 220°. On oxidation with MnO_4K it yields pyro-racemic acid and iso-propyl-succinic acid (B. **33**, 2457). With PCl_5 it gives monochloro-phellandrene $C_{10}H_{16}Cl$, b.p.$_{15}$ 108°, which, with zinc dust and methyl alcohol, is reduced to α-phellandrene (B. **38**, 1832).

Pulegon, $\Delta^{4(8)}$-*menthene-3-ketone* $CH_3.CH\langle^{CH_2\text{—}CO}_{CH_2\text{—}CH_2}\rangle C{=}C(CH_3)_2$, b.p. 221°, D 0·936, n_D=1·4846, is contained in the ethereal oil of *Mentha pulegium* and *Hedeoma pulegioides*, which are sold under the name polei oil. By the addition of hydrogen, pulegone is converted into menthone; by oxidation, into β-methyl-adipinic acid and acetone; and by heating with formic acid or with water under pressure, into acetone and 3-methyl-cyclo-hexanone, which on oxidation also yields β-methyl-adipinic acid:

$$CH_3.CH\langle^{CH_2\text{—}CO}_{CH_2\text{—}CH_2}\rangle C:(CH_3)_2 \xrightarrow{2H} CH_3CH\langle^{CH_2\ CO}_{CH_2.CH_2}\rangle CH.CH(CH_3)_2$$

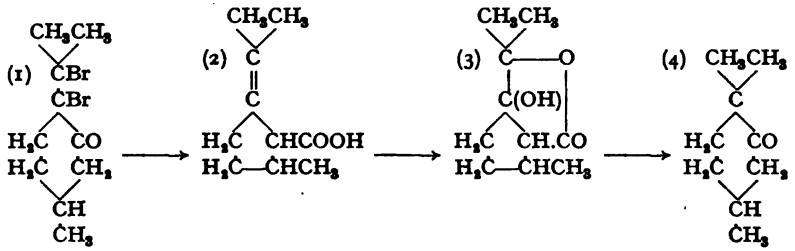
$$\downarrow$$

$$CH_3.CH\langle^{CH_2\text{—}CO}_{CH_2\text{—}CH_2}\rangle CH_2 \xrightarrow{O} CH_3CH\langle^{CH_2\text{—}COOH}_{CH_2\text{—}CH_2}\rangle COOH.$$

If, on the other hand, methyl-cyclo-hexanone and acetone are

condensed, by means of alkalies, we obtain a geometrically isomeric pulegone boiling at 215° (A. **300**, 267).

If pulegone dibromide (1) is boiled with sodium methylate solution, we get **pulegenic acid** (2) $C_{10}H_{16}O_2$, in which case the six-membered ring system is probably converted into a five-membered system. Oxidation with potassium permanganate converts the pulegenic acid into an oxy-lactone (3), which on heating with half-saturated sulphuric acid is converted into pulenone (4) or 3, 6, 6-trimethyl-cyclo-hexanone, with elimination of CO_2 and ring expansion, and an atomic displacement quite analogous to the pinacolin transposition (A. **329**, 82; cp. also A. **376**, 154):



From pulegenic acid the hydrocarbon pulegen C_9H_{16}, b.p. 139°, D 0·791, is formed by rejection of CO_2. Its nitroso-chloride can be converted into pulegenone $C_9H_{14}O$, b.p. 190°, a ketone closely related to camphor-phorone (A. **327**, 125).

Pulegone combines, like other $\alpha\beta$-unsaturated ketones, with sodium-malonic ester (A. **345**, 158, 188) and potassium cyanide (C. 1907, I. 721).

Benzylidene-pulegone, b.p. 203° (A. **305**, 267): by the action of hydroxylamine upon pulegone in the presence of alkali, we obtain iso-pulegone-oxime with displacement of linkage. Under other conditions we obtain the hydroxylamine addition product, **pulegone-hydroxylamine** $C_{10}H_{17}O(NHOH)$, m.p. 157°, which yields on oxidation nitroso-menthone, m.p. 35°, and by reduction amido-menthone (B. **31**, 1809; **32**, 3365), as well as **pulegone-hydroxylamine-oxime** $C_{10}H_{17}(NHOH)(:NOH)$, m.p. 118°, which is reduced with sodium and alcohol to 3, 8-diamido-menthane (B. **38**, 146).

Iso-pulegone, $\Delta^{8(9)}$-*menthene*-3-*ketone* $CH_3CH\langle\begin{matrix}CH_2—CH\\CH_2—CH_2\end{matrix}\rangle CHC\langle\begin{matrix}\\CH_2\end{matrix}\!\!=\!\!\begin{matrix}CH_2\\CH_2\end{matrix}$, b.p.$_{14}$ 103°, is obtained from its oxime, m.p. 120°, on heating with oxalic acid (A. **365**, 24), from pulegone hydrobromide with basic lead nitrate, or by oxidising its alcohol, iso-pulegol, the isomeric product of citronellal. It contains two unsym. C atoms, and therefore occurs in several geometrically isomeric optically active modifications. By treatment with baryta water it is converted back into pulegone (B. **32**, 3357).

2-Oxy-Δ^1-menthene-3-ketone $CH_3C\langle\begin{matrix}C(OH)—CO\\CH_2—CH_2\end{matrix}\rangle CH.CH\langle\begin{matrix}CH_2\\CH_2\end{matrix}$, m.p. 84°, b.p.$_{10}$ 110°, is probably represented by the *bucco-camphor* or *diosphenol* obtained from bucco leaves (*Barosma*). In its behaviour it shows both ketone and phenol character. With ferric chloride it gives a green coloration, it has an acetate and a benzoate, forms with phenyl-iso-cyanate a phenyl-urethane, m.p. 41°, and with hydroxyl-

amine a monoxime, m.p. 125°. On heating with concentrated HCl it is converted into thymol, and a little carvacrol. On oxidation with ozone we obtain α-iso-propyl-γ-acetyl-butyric acid; and on reduction with sodium and alcohol, 2, 3-dioxy-hexahydro-cymol, which is oxidised by permanganate to α-methyl-α-iso-propyl-adipinic acid. Synthetically, bucco-camphor is formed by oxidation of oxy-methylene-menthone with ozone (B. **39**, 1158).

(*c*) **Menthadiene-ketones,** *keto-dihydro-p-cymols* $C_{10}H_{14}O$.—The most important member of this group is *carvone*, formerly called *carvol*. Its importance is due to its intimate relationship to carvacrol and limonene, which are isomeric with it. Carvone is known in three modifications, the d-, l-, and [d+l]-.

d-Carvone $CH_3.C\begin{matrix}CO.CH_2\\CH.CH\end{matrix}\!\!>\!\!C.CH(CH_3)_2$ (B. **28**, 31), or

$CH_3.\dot{C}H\begin{matrix}CO.CH\\CH{=}CH\end{matrix}\!\!>\!\!C.CH(CH_3)_2$, or $CH_3.C\begin{matrix}CH.CH_2\\CO.CH_2\end{matrix}\!\!>\!\!\dot{C}H.C\begin{matrix}CH_3\\CH_3\end{matrix}$ (?)

(B. **28**, 2145), $[\alpha]_D = +62°$, boiling at 225°, occurs in carraway oil and in dill oil. When heated with potassium hydroxide or phosphoric acid it changes to isomeric carvacrol or 2-methyl-5-iso-propyl-oxy-benzol; hence it is assumed that in carvone the CO group, like the OH group in carvacrol, is in the ortho-position with reference to the methyl group. With PCl_5 carvone forms a dichloride $C_{10}H_{14}Cl_2$, which on distillation with quinolin yields 2-chloro-cymol (B. **32**, 2555). Reduction changes it to dihydro-carveol, while ammonium formate converts it into dihydro-carvylamine. Potassium permanganate oxidises carvone to *oxy-terpenylic acid* $C_8H_{12}O_5$, which easily changes to a dilactone $C_8H_{10}O_4$, melting at 129° (B. **27**, 3333; **28**, 2148). The carvones combine with hydrogen sulphide, hydrogen chloride, hydrogen bromide, and bromine (B. **28**, R. 548; A. **305**, 235; C. 1907, I. 568). On the splitting up of carvone tribromide to **carvenolidene** $C_{10}H_{14}O_2$, see A. **305**, 245. With sodium bisulphite we obtain the sodium salt of carvone dihydro-sulphonic acid (C. 1900, I. 1155). On shaking up with dilute H_2SO_4, carvone takes up one molecule H_2O and forms oxy-dihydro-carvone (carvone hydrate, B. **38**, 1719; **39**, 677).

With aceto-acetic ester carvone combines in the presence of sodium alcoholate to a dicyclic condensation product (B. **36**, 225).

l-Carvone, $[\alpha]_D = -60°$, boiling at 230°, occurs in mint oil and curomoji oil (B. **24**, 81). It is obtained pure by distilling its hydrogen sulphide compound, melting at 187°, with caustic potash (A. **305**, 224).

[d+l]-Carvone, boiling at 230°, is formed on mixing d- and l-carvone, as well as by oxidising carveol-methyl ether. Formation from terpineol, B. **29**, R. 587.

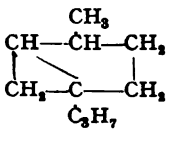
The three carvones are linked through the three carvoximes to the three corresponding limonenes. The carvoximes are prepared not only by the action of hydroxylamine upon the carvones, but also upon boiling the limonene nitroso-chlorides with alcoholic potash. d-Carvone and l-limonene correspond on the one side to each other, while on the other l-carvone and d-limonene correspond, inasmuch as l-limonene nitroso-chloride yields d-carvoxime, and d-limonene nitroso-chloride l-carvoxime.

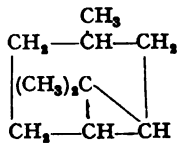
d-Carvoxime, $[\alpha]_D = +39{\cdot}71°$, and **l-carvoxime,** $[\alpha]_D = -39{\cdot}34°$, melt at 72°. **[d+l]-Carvoxime** melts at 33°, and is obtained from dipentene nitroso-chloride. Concentrated sulphuric acid rearranges carvoxime to p-amido-thymol (compare rearrangement of β-phenyl-hydroxylamine to p-amido-phenol, A. **279,** 366). **Hydroxylamino-carvoxime** $C_{10}H_{15}(NOH).NHOH$, a syrup, oxidises to form *the di-oxime of a diketone* $C_{10}H_{14}O_2$, m.p. 185°–187°, which is also formed direct from carvone by atmospheric oxidation in the presence of baryta, and is probably 1, 4-*methyl-iso-propenyl-dihydro-resorcin* (B. **34,** 2105).

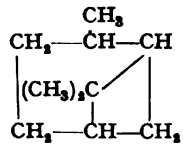
C. Dicyclic Terpene Group.

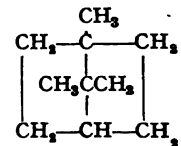
The terpenes of this group are distinguished from the monocyclic terpenes by the fact that they can only add two univalent atoms or atomic groups. They therefore contain two carbon rings. These dicyclic terpenes, and their derivatives containing oxygen, are joined up with the monocyclic terpene compounds by numerous transitions. Like the latter, they are closely related to p-cymol, and can usually be converted into this with facility.

Their dihydro-compounds are derived from hexahydro-cymol either by joining two carbon atoms in the m-position towards one another, by a diagonal link, thus forming a compound of the trimethylene and pentamethylene group. This gives the sabinane or tanacetane group. Or, the tertiary carbon atom of the iso-propyl group is joined with a second carbon atom of the hexamethylene ring. According as to whether this link occurs in the o-, m-, or p-position, we get the fundamental hydrocarbons of the carane, pinane, and camphane groups:


Sabinane


Carane


Pinane


Camphane.

While these nuclear and bridge-linkages are stable as regards the usual addition-reactions, and are thus clearly distinguished from double linking, they are broken up with extraordinary facility by the action of higher temperatures, but especially by hydrating agents, giving rise to derivatives of the monocyclic terpenes.

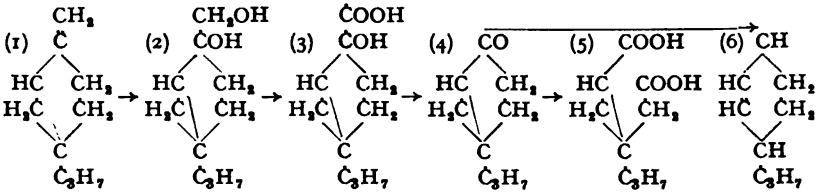
I. Sabinane or Tanacetane Group.

The closely related compounds of this group, the most important representative of which is thujone or tanacetone, contain a compound trimethylene and pentamethylene ring, and can be broken down by oxidation into trimethylene-carboxylic acids.

1. **Hydrocarbons.**—Sabinene and the two thujenes belong to these. All three contain the same carbon skeleton, and only differ by the position of the double linkage, since by gentle reaction they can be transformed into the equally saturated dicyclic hydrocarbon $C_{10}H_{18}$, *i.e.* sabinane or thujane (C. 1911, I. 313).

Sabinene (1) $C_{10}H_{16}$, b.p. 163°–165°, D_{20} 0·842, n_D 1·468, has been

found in its dextro-rotatory form in Ceylon cardamom oil, majoran oil, and pilea oil (A. **357,** 77 ; B. **40,** 2963). With quite dry HCl in CS_2 solution it yields terpinene monochlorohydrate, with glacial acetic halogen hydride the corresponding terpinene-dihydro-haloids. By dilute H_2SO_4 it is converted, in the cold, into optically active terpinenol-4 and terpinene-terpin, and with heat into α-terpinene. On oxidation with $KMnO_4$, sabinene behaves like most other terpenes with semi-cyclically linked methylene group (cp. β-pinene and camphene). Sabinene-glycol (2) is first formed, m.p. 54°, which is then oxidised to an α-oxy-acid marked by its sparingly soluble sodium salt, viz. sabineric acid (3), m.p. 57°, and further to sabina-ketone (4), b.p. 212°, containing one C atom less. The latter, on heating with aqueous or alcoholic H_2SO_4, easily splits the trimethylene ring, and forms Δ^2-iso-propyl-cyclo-hexenone (6), and on further disintegration α-tanacetone-dicarboxylic acid (5) (A. **359,** 266 ; B. **35,** 2045) :



As already mentioned, sabina-ketone may be used for building up β-terpinene.

α-Thujene $CH_3C\langle\begin{matrix}CH—CH_2\\CH—CH_2\end{matrix}\rangle CC_3H_7$, b.p. 152°, D_{20} 0·8275, n_D 1·4504, and **β-thujene** $CH_3CH\langle\begin{matrix}CH=CH\\CH—CH_2\end{matrix}\rangle C.C_3H_7$ (?), solid, b.p. 150°, D_{20} 0·8248, n_D 1·4484, have been obtained by distillation from the methyl-xanthogenate of thujyl alcohol, and from thujylamine by thorough methylation and by heating the resulting quaternary ammonium base (B. **34,** 2276 ; **37,** 1481). On oxidation with $KMnO_4$ α-thujene yields α-thuja-keto-acid (see below), and combines, with two molecules halogen hydride, to form the corresponding terpinene-dihalogen hydrates. On shaking up with dilute sulphuric acid it becomes, like sabinene, active terpinenol-4 and terpinene-terpin (A. **350,** 166 ; **356,** 201). Isomeric with these two hydrocarbons is iso-thujene, b.p. 172°–175°, D 0·840, n_D 1·476, formed by the dry distillation of thujylamine-chlorohydrate (A. **286,** 99).

Sabinane, *thujane,* $C_{10}H_{18}$, b.p. 157°, is formed by the reduction of sabinene, α- and β-thujene, with hydrogen in the presence of platinum black (C. 1911, I. 313).

2. **Alcohols.—Sabinene hydrate,** *methyl-sabina-ketol* $CH_3\rangle HO\rangle C\langle\begin{matrix}CH_2—CH_2\\CH—CH_2\end{matrix}\rangle C.C_3H_7$, m.p. 39°, b.p. 195°–201°, is formed besides α-terpinene by the action of methyl-magnesium iodide upon sabina-ketone. With glacial acetic hydrogen bromide it forms terpinene-dibromo-hydrate, and, on shaking up with dilute sulphuric acid, an optically active terpinenol-4 and terpinene-terpin (A. **357,** 64).

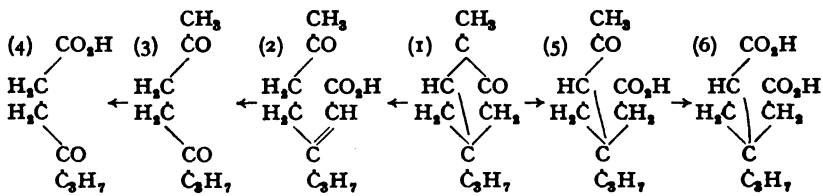
Thujyl-alcohol, *tanacetyl-alcohol* $CH_3CH\langle\begin{matrix}CHOH—CH_2\\CH——CH_2\end{matrix}\rangle C.C_3H_7$, b.p.$_{13}$

92·5°, D 0·9249, n_D 1·4635, is formed by reduction of thujone or tanacetone, into which it reverts on oxidation. It is found, partly free and partly in the form of aliphatic esters, in wormwood oil (A. **272,** 109).

Sabinol $CH_2=C<\begin{matrix}CH(OH)—CH_2\\ CH———CH_2\end{matrix}>C.C_3H_7$, b.p. 211°, D_{20} 0·9432, an unsaturated secondary alcohol, found in the form of its ester in *oleum sabinæ*. It is converted into cymol by dehydrating agents, into tanacetone by short heating with zinc dust, and into tanacetyl-alcohol by reduction with sodium and alcohol. Careful oxidation with $KMnO_4$ converts it into **sabinyl-glycerin** $C_{10}H_{15}(OH)_3$, m.p. 153°, which easily passes into cumin-alcohol by splitting off water; strong oxidation produces α-tanacetone-dicarboxylic acid (B. **38,** 1191, 1459; cp. also A. **360,** 98).

3. **Amines.—Thujylamine** $C_{10}H_{17}NH_2$, b.p. 195°, by reduction of thujone oxime. On heating its chlorohydrate it yields iso-thujene.

4. **Ketones.—Thujone,** *tanacetone* (1) $C_{10}H_{16}O$, b.p. 200°, D 0·917, n_D=1·4511, is found in two physically isomeric forms—the lævo-rotatory α-thujone, $[\alpha]_D=-10·23°$, semi-carbazone, m.p. 186°, oxime liquid, chiefly in thuja oil; the dextro-rotatory β-thujone, $[\alpha]_D=+76·16°$, semi-carbazone, m.p. 171° and 175°, oxime, m.p. 55°—chiefly in the oil of *Tanacetum vulgare*. Mixtures of both forms have been traced in wormwood oil, sage oil, absinth oil, and the oil of *Artemisia Barrelieri* (A. **336,** 247). On oxidation with $KMnO_4$ both forms give the chemically isomeric α- and β-**thuja** or **tanaceto-ketone-carboxylic acids** $CH_3CO.C_7H_{12}.COOH$, m.p. 75° and 78°, the α-acid being saturated and the β-acid unsaturated. On heating, the α-acid turns into the β-acid, the latter (2) being oxidised into a diketone (3), and then converted into δ-dimethyl-lævulinic acid (4). The α-tanaceto-ketonic acid (5) is broken down, by bromine and alkali, to **α-tanacetone-dicarboxylic acid** (6) $C_9H_{14}O_4$, m.p. 142°, a saturated dibasic acid, which easily turns into anhydride, and is also formed by the oxidation of sabinol, sabinene, and α-thujene:



Condensation with benzaldehyde converts thujone into **benzylidene-thujone,** b.p.$_9$ 178°, which is split up by potassium permanganate into benzoic acid and **homo-tanacetone-dicarboxylic acid** $C_{10}H_{16}O_4$, m.p. 148°. This acid, like α-tanacetone-dicarboxylic acid, and tanacetone itself, probably contains the trimethylene ring (B. **36,** 4367; but see B. **38,** 1192).

Thujone, treated with alcoholic sulphuric acid, turns into iso-thujone. On heating to 280°, it turns into *carvo-tanacetone.* These two ketones are unsaturated, in contrast with thujone (B. **28,** 1959). **Thujone-oxime,** m.p. 54°, with alcoholic sulphuric acid, turns into carvacryl-amine (B. **30,** 325); treatment with PCl_5 converts it into the lactame-like thujone-isoxime, m.p. 90° (A. **336,** 270).

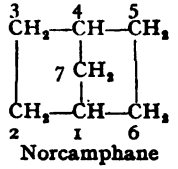
Iso-thujone $CH_3.C\begin{matrix}CO\text{——}CH_2\\ \diagdown C(CH_3).CH.CH(CH_3)_2\end{matrix}$ (?), b.p. 231°, D 0·927, n_D= 1·4822, m.p. 119°. α- and β-Semi-carbazone, m.p. 208° and 148°. Oxime, m.p. 120°. Benzylidene-iso-thujone ($C_{10}H_{14}O$) : CHC_6H_5, m.p. 83°. When oxidised, iso-thujone yields a **keto-lactone** $C_{10}H_{16}O_3$, and, further, **β-iso-propyl-lævulinic acid** $CH_3COCH(C_3H_7).CH_2COOH$; by reduction a saturated alcohol is obtained, **thuja-menthol,** *dihydro-iso-thujol* $C_{10}H_{19}OH$, b.p. 212°, D 0·9015, n_D=1·4636, which, on oxidation with chromic acid, forms **thuja-menthone** $C_{10}H_{18}O$, b.p. 208°, D 0·891, n_D 1·447. Oxime, m.p. 95° ; isoxime, m.p. 117°. All these compounds are probably derivatives of cyclo-pentane (A. **323,** 348 ; **336,** 276 ; B. **28,** 1958).

Umbellulone $CH_3.C\begin{matrix}CH\text{——}CO\\ \diagdown CH\text{——}CH_2\end{matrix}\diagup C.C_3H_7$, b.p.$_{10}$ 93°, $[\alpha]_D$−37°, which occurs in profusion in the leaves of Californian laurel, *Umbellularia californica.* Semi-carbazone, m.p. 242°. On heating to 280°, it transposes into thymol. Bromination and subsequent distillation produce p-cymol and other brominated bodies. Sodium and alcohol reduce it to the saturated alcohol $C_{10}H_{17}.OH$, b.p.$_{10}$ 90°, which, on oxidation with chromic acid, turns into **dihydro-umbellulone** $C_{10}H_{16}O$, b.p.$_{10}$ 85°. The benzylidene compound of the latter, on oxidation with $KMnO_4$, yields, like benzylidene-thujone (see above), **l-homo-tanacetone-dicarboxylic acid** (B. **40,** 5017 ; **41,** 3988).

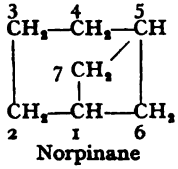
Carane, Pinane, and Camphane Group.

The derivatives of this group contain, as already stated, a hexamethylene ring, in which two carbon atoms in the o-, m-, or p-position are joined together by means of a carbon bridge. In nature such compounds have only been found with an m- or p-bridge. Among the former we have pinene, extremely frequent in natural substances; and among the latter we have camphor, the most important derivative in this group, and the closely related fenchone, as well as the derived terpenes, camphene and fenchene. Characteristic of the compounds of this group is the remarkable facility with which they undergo intramolecular transpositions under the influence of acid reagents. These transpositions are sometimes accompanied by a complete change in the ring system, which makes a recognition of the connection between the products and the elucidation of their constitution extremely difficult.

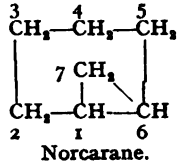
Nomenclature.—The names are mostly derived from botany, and associated with the extraction of some of the more important substances. Only in a few cases does a systematic nomenclature appear possible. Thus, the hitherto unknown demethylated hydrocarbon corresponds to the three chief types of these groups, and designated by ***nor-camphane, nor-pinane,*** and ***nor-carane,*** which are used as bases, and their carbon atoms are given numbers as follows :



Norcamphane



Norpinane



Norcarane.

II. Carane Group.

The compounds of this group are ranged with the sabinane group, since they also contain a trimethylene ring, which, however, is combined with a hexamethylene ring. Hydrocarbons of this group, which has only been investigated by synthesis, are unknown.

Carone (formula below), b.p.$_{15}$ 100°, is formed from dihydro-carvone hydrobromide with alcoholic potash. It is comparatively stable towards potassium permanganate, which only attacks it at water-bath temperature, and oxidises it to caronic acid, or 1, 1-dimethyl-2, 3-trimethylene-dicarboxylic acid (1). On the other hand, the trimethylene ring of carone can be split up in three different places: (1) Splitting between C_6 and C_7; on heating to about 210° carone transposes into carvenone (2) (B. **32,** 1222); HBr turns it into dihydro-carvone hydro-bromide, and sulphuric acid into oxy-tetrahydro-carvone. (2) Splitting between C_1 and C_7; the carylamine $C_{10}H_{17}NH_2$, stable in the presence of $KMnO_4$, obtained from carone-oxime, m.p. 78°, by reduction transposes, in the presence of HCl, into the isomeric unsaturated vestrylamine (3), whose chlorohydrate, on heating, yields carvestrene (B. **27,** 3486). (3) Splitting between C_1 and C_6; the **cyano-carone** $C_{10}H_{15}(CN)O$, m.p. 55°, obtained from cyano-dihydro-carvone hydro-bromide with alcoholic potash, which can also be disintegrated to caronic acid, yields, on heating with alcoholic potash, *eucarvone* (C. 1910, I. 924).

An **oxy-carone** $C_{10}H_{16}O_2$, b.p.$_{19}$ 135°, has been obtained by starting from dihydro-carvone dibromide; the latter, with soda, yields oxy-bromo-tetrahydro-carvone, which, on treatment with methyl-alcoholic potash, turns into oxy-carone; on digesting the latter with dilute sulphuric acid it is turned into a ketone derivative of terpin (B. **31,** 3208).

A constitution and transformations similar to those of carone are shown by pseudo-phenyl-acetic acid, or nor-caradiene-carboxylic acid, obtained from benzol and diazo-acetic ester.

Eucarvone (formula 4 above), b.p.$_{12}$ 86°, $D_{20}=0{\cdot}952$, $n_D=1{\cdot}5048$ (A. **339,** 94), probably belongs to the heptacarbocyclic compounds, but is treated here on account of its relation to carone. It is formed from carvone hydro-bromide with alcoholic potash, evidently with intermediate formation of the unstable $\alpha\beta$-unsaturated carone (cp. the transition of cyano-carone into eucarvone). It is optically inactive. On boiling down with methyl-alcoholic potash, it gives a deep-blue unstable coloration. Semi-carbazone, m.p. 184°; oxime, m.p. 106°; oxamino-oxime, m.p. 142° (A. **330,** 275). It unites with benzaldehyde to form benzylidene-eucarvone, m.p. 113°. On oxidation it yields acetic acid and unsym. dimethyl-succinic acid. On reduction with Na and alcohol we get, simultaneously, **dihydro-eucarveol** $C_{10}H_{17}OH$, b.p.$_{21}$ 109°, and **tetrahydro-eucarveol** $C_{10}H_{19}OH$, b.p. 220°, which, on oxidation, turn into the corresponding ketones.

Dihydro-eucarvone $C_{10}H_{16}O$, b.p.$_{14}$ 87° (B. **28,** 646), and **tetrahydro-eucarvone** $C_{10}H_{18}O$, b.p.$_{13}$ 91°–93° (B. **31,** 2071). The latter, with chromic acid, gives a ketonic acid $C_{10}H_{18}O_3$, from which potassium hypobromite forms a $\beta\beta$-dimethyl-pimelinic acid, indicating the existence of a chain of seven members.

On prolonged heating eucarvone turns into carvacrol; PCl_5 produces 2-chloro-cymol. The unsaturated diamine, obtained from the oxamino-oxime of eucarvone by reduction, yields p-cymol by the distillation of its phosphate. In this case, we must assume the intermediate formation of a cyclo-heptatriene derivative, which transposes into the more stable benzene derivative.

Dihydro-eucarvylamine $C_{10}H_{17}NH_2$, b.p.$_{40}$ 117°, from eucarvoxime; its chlorohydrate yields *euterpene* on heating (A. **305**, 239). *Tetrahydro-eucarvylamine* $C_{10}H_{19}NH_2$, b.p. 210° (A. **339**, 115).

III. Pinane Group.

Hydrocarbons.—**Pinene.**—Pinene is extremely frequent among the ethereal oils and is the chief ingredient of the turpentine oils obtained from the different varieties of pine. It also occurs in many other ethereal oils—eucalyptus, juniper-berry, sage, etc.

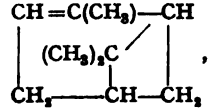
Turpentine Oil.—Turpentine, the resinous juice exuding from various Coniferæ, consists of a solution of resins in turpentine oil which distils with steam, while the resin (colophony) remains behind. Turpentine oil is a colourless liquid, boiling at 158°–160°, with specific gravity of 0·856–0·87. Its peculiar odour is due to the aldehyde-like oxidation products (B. **29**, R. 871) produced by the action of sunlight.

It is almost insoluble in water, but is miscible with absolute alcohol and ether. It dissolves phosphorus and rubber, and serves for the preparation of varnishes and oil-colours.

The turpentine oils, according to their origin, are distinguished by different rotatory powers.

The American, Algerian, and Greek turpentine oils contain chiefly d-pinene, the French and Spanish oils l-pinene. Besides these, dextro- and lævo-rotatory pinenes are found in various ethereal oils, such as eucalyptus oil, hawthorn (?) oil, sage oil, etc.

In most cases pinene is accompanied by small quantities of a closely related terpene of higher boiling-point, which, with HCl, gives the same chlorohydrate, but is distinctly different from it in its oxidation products. This is especially the case in the oils of turpentine, and the related body is distinguished as β-pinene from the ordinary or α-pinene.

[d+l]-α-Pinene  , b.p. 155°, D_{20} 0·858, n_D= 1·46553 (21°).

d-α-Pinene is obtained by fractional distillation of American turpentine oil, while l-α-**pinene** is obtained from French turpentine oil, but not chemically pure. For obtaining pure α-pinene it is converted into the easily purified nitroso-chloride (β-pinene gives no addition product with nitroso-chloride), and is thus liberated with the help of aniline, or by boiling with sodium acetate and glacial acetic acid. It is thus obtained pure, but always inactive. Artificially, l-α-pinene has been obtained by heating nopinol-acetic acid, and d-α-pinene by the

dry distillation of methyl-xanthogenate from pino-campheol (A. **368,** 1; C. 1908, I. 1179).

Pinene has one double link. It combines with 2Cl or 2Br to form compounds which on heating disintegrate into hydrogen haloid and p-cymol. By the action of moist hydrogen haloids, pinene is converted into dipentene dihydro-haloids, while with perfectly dry hydrogen haloids in the cold, monohalogen hydrates are obtained. These, however, like the halogen addition products, no longer contain the pinene ring, the hydrogen haloid having produced a complete change in the ring system, giving rise to borneol derivatives. Thus the pinenic hydro-haloids are identical with the bornyl haloids. In the same way the treatment of pinene with organic acids, such as oxalic acid, salicylic acid, trichloracetic acid, etc., produces esters of borneol, or of the stereo-isomeric iso-borneol. This easy transition of pinene into borneol, and iso-borneol, has been industrially utilised for the artificial production of camphor from oil of turpentine. The action of dilute nitric or sulphuric acid upon pinene produces terpine hydrate, while, with sulphuric acid and glacial acetic acid, or benzol-sulphonic acid (C. 1909, II. 25), the primary hydration product α-terpineol can be isolated. On heating to 250°–270° pinene is converted into dipentene.

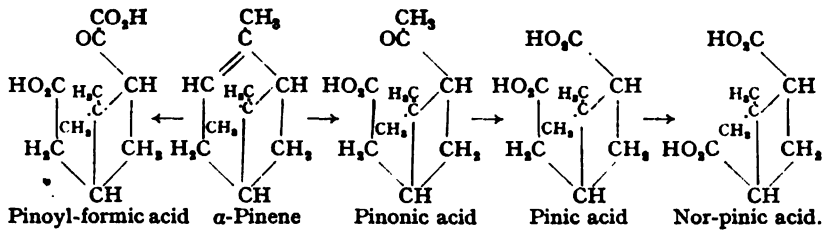
The oxidation products of pinene have been examined in some detail. In air, oil of turpentine gradually absorbs oxygen with the formation of peroxides (B. **31,** 3046), and resinifies with formation of certain quantities of formic acid, acetic acid, and cymol. On the formation of pinol hydrate from pinene in air and sunlight, see below. Strong oxidising agents, such as nitric acid, produce terebinic acid, p-toluic acid, terephthalic acid, etc. Chromic acid mixture produces terpenylic acid as a main product.

Oxidation with mercuric acetate produces a racemic sobrerol, which is further oxidised to oxy-dihydro-carvone or carvone hydrate. From the latter, on heating with oxalic acid, water is eliminated, with formation of carvone and carvacrol, and, on further oxidation with potassium permanganate, terpenylic acid (C. 1909, I. 1561).

By careful oxidation of pinene with potassium permanganate, we first obtain **α-pinene-glycol** $C_{10}H_{16}(OH)_{21}$, b.p.$_{14}$ 146° (B. **27,** 2270), and then a keto-monocarboxylic acid called **pinonic acid** $C_{10}H_{16}O_3$, m.p. 70° (active) and m.p. 104° (inactive), b.p.$_{15}$ 187° (C. 1909, II. 2158). There are also small quantities of a ketone-dicarboxylic acid, **pinoyl-formic acid** $C_{10}H_{14}O_5$, m.p. 79°. The pinene ozonide, obtained by the action of ozone upon pinene, also yields pinonic acid in the decomposition with water (B. **40,** 138).

On oxidising the very unstable pinonic acid with bromine, or alkali, or with dilute nitrous acid, we obtain the **stable pinic acid** $C_9H_{14}O_4$, m.p. 102°, and from this, through α-bromo- and α-oxy-pinic acid, and oxidation of the latter, we obtain **nor-pinic acid** $C_8H_{12}O_4$, m.p. 174°. The two latter very stable acids probably contain a tetramethylene ring.

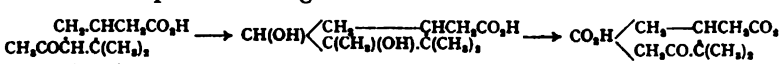
Baeyer, therefore, in agreement with Wagner, assumes for pinonic acid and pinene the presence of a 4-member so-called piceane ring (B. **29,** 2776). The course of the oxidation is illustrated in the following scheme:



Pinoyl-formic acid α-Pinene Pinonic acid Pinic acid Nor-pinic acid.

The decomposition of pinonic acid and pinoyl-formic acid has also been accomplished in other ways.

(1) By means of chromic acid, **keto-iso-camphoric acid** has been obtained from pinonic acid, and also by oxidation of campholinic acid. The keto-iso-camphoric acid can be disintegrated into **iso-camphoronic acid** $CO_2HC(CH_3)_2CH(CH_2CO_2H)_2$ (synthesis, C. 1901, I. 221), and further to **dimethyl-tricarballylic acid** $COOHC(CH_3)_2CH(COOH)CH_2COOH$. The constitution of the latter acid is proved by the splitting up of the corresponding oxy-acid (B. **30**, 1959) on fusing with potash in dimethyl-succinic acid and oxalic acid. The peculiar formation of keto-iso-camphoric acid from pinonic acid can, according to modern ideas (cp. B. **32**, 2080), be interpreted in a sense that the 4-member piceane ring of pinonic acid takes up water and is converted into the 5-member camphoceane ring :



Pinonic acid α-Dioxy-dihydro-campholenic acid Keto-iso-camphoric acid.

(2) On heating with acids, pinonic acid undergoes an intermediate hydrolytic splitting, and then a transposition into **homo-terpenylic-methyl-ketone** [*metho-ethyl-heptanonolide*] $(CH_3)_2\overline{C.CH.CH_2.COO}$ $\overline{CH_2.CH_2.CO.CH_3}$, which we have learnt to regard as a disintegration product of terpineol. Similarly, pinoyl-formic acid is transposed into **homo-terpinoyl-formic acid** $(CH_3)_2\overline{C.CH.CH_2.COO}$ $\overline{CH_2.CH_2.CO.COOH}$. These transposition products on further oxidation yield :

Homo-terpenylic acid $(CH_3)_2\overline{C.CH.CH_2.COO}$ $\overline{CH_2.CH_2.COOH}$

Terpenylic acid $(CH_3)_2\overline{C.CH.CH_2.COO}$ $\overline{CH_2COOH}$

Terebinic acid $(CH_3)_2\overline{C.CH.CH_2.COO}$ $\overline{COOH}$

Terebinic acid $C_7H_{10}O_4$, melting at 175°, was first obtained by oxidising turpentine oil with nitric acid; it is also produced in the oxidation of terpenylic acid with potassium permanganate, or of iso-propyl-succinic acid with chromic acid. Synthetically, it is prepared by the condensation of acetone and bromo-succinic ester with zinc-copper, or by the action of CH_3MgI upon aceto-succinic ester (C. 1907, I. 1202). See also Teraconic acid (B. **29**, 933; C. 1898, I. 558; 1899, I. 1158) It behaves analogously to the paraconic acids. When heated it loses

carbon dioxide and becomes **pyro-terebinic acid** $(CH_3)_2C:CHCH_2COOH$, together with **iso-capro-lactone** and **teraconic acid** $(CH_3)_2C:C(COOH)CH_2.COOH$, from which it can be re-formed by digestion with mineral acids. Baryta water converts terebinic acid into the crystallising barium salt of diaterebinic acid or oxy-iso-propyl-succinic acid.

By oxidation with HNO_3, terebinic acid is turned into **dicarboxy-valero-lactonic acid** $COOH.\overline{C(CH_3)CH(COOH)CH_2CO}\overline{O}$ (B. **32**, 3662). See the formation of terebinic acid from caronic acid.

Terpenylic acid $C_8H_{12}O_4$ melts at 90° when anhydrous. It is obtained by oxidising turpentine oil with a chromic acid mixture, and homo-terpenylic acid with nitric acid (B. **29**, 2789).

Synthetically it has been obtained by the action of CH_3MgI upon β-acetyl-glutaric ester (C. 1907, I. 1202).

Upon distillation it yields **teracrylic acid** $(CH_3)_2C:CH(CH_3)CH_2.COOH$. Terpenylic acid, by reduction, becomes *β-iso-propyl-glutaric acid* (see B. **29**, 920, 2621).

Homo-terpenylic acid $C_9H_{14}O_4$, melting at 102°, results when homo-terpenyl-formic acid is oxidised with nitric acid or with lead oxide (B. **29**, 1916). It is synthesised by means of CH_3MgI and β-acetyl-adipinic ester (C. 1907, I. 1202).

The oxidation of pinene to pinonic acid and the hydrolytic re-arrangement of the latter to homo-terpenylic methyl-ketone is certainly to be regarded as the reverse of the processes which take place in the hydrolytic rearrangement of pinene into terpin hydrate, terpineol, and the oxidising decomposition of the latter into homo-terpenylic methyl-ketone (above).

d-Pinene hydrochloride, smelling of camphor, and therefore formerly called *artificial camphor*, $C_{10}H_{17}Cl$, melting at 125° and boiling at 208°, is formed on conducting dry hydrochloric acid gas into well-cooled pinene. It is a white crystalline mass, with an odour like that of camphor. The hydrochloride from d-pinene is optically inactive, while the l-pinene hydrochloride is lævo-rotatory, $[\alpha]_D = -30°$. **Pinene hydrobromide** melts at 40° (A. **227**, 282).

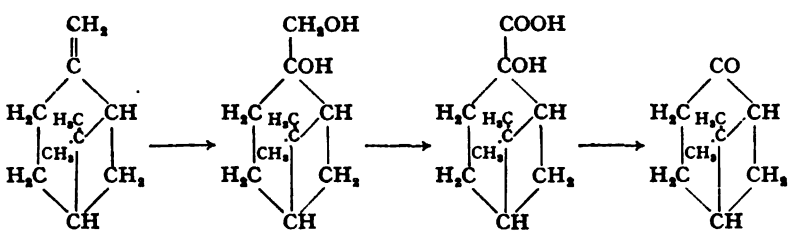
Pinene hydro-iodide $C_{10}H_{17}I$, b.p.$_{15}$ 119°. The pinene hydrohaloids are identical with the bornyl haloids. This follows from the fact that the Mg compound $C_{10}H_{17}MgCl$, obtained by the action of Mg upon pinene chlorohydrate in ether solution, turns into camphane by decomposition with water, and into borneol by the action of oxygen (B. **39**, 1127). During the action of the halogen hydrides upon pinene there is, therefore, a "sliding" of the dimethyl-methylene bridge, from the m-position into the p-position. By a quite analogous displacement of the methylene group of the piceane ring, we obtain the derivatives of fenchyl alcohol. This explains the secondary formation of fenchyl chloride in the action of HCl upon pinene. The elimination of HCl from pinene chlorohydrate, which is attended by much difficulty, produces camphene. This transition also is the result of a far-reaching transposition. Hypochlorous acid attaches itself to pinene with dissolution of the double linking, and of the four-membered piceane ring. The action of alkalies upon the resulting dichloro-hydrins $C_{10}H_{18}O_2Cl_2$ has been made to produce pinol oxide, sobrerythrite, pinol-chlorohydrin, and other bodies (B. **32**, 2064).

Pinene dibromide $C_{10}H_{16}Br_2$, m.p. 170°, by the action of bromine upon pinene, in carbon tetrachloride (A. **264**, 1). Like pinene chlorohydrate, it probably also belongs to the camphor type, being reduced to camphane by Na and alcohol (B. **33**, 3423). On treatment with zinc dust it yields a terpene, isomeric with pinene and camphene, m.p. 67°, b.p. 153°, containing apparently no double link, a so-called tricyclene.

Pinene nitroso-chloride, melting at 115°, is obtained by means of nitrosyl chloride, or amyl nitrite, glacial acetic acid, and hydrochloric acid. Hydrogen chloride in ether, when allowed to stand in contact with it, produces, just like limonene nitroso-chloride, hydrochlorocarvoxime (B. **29**, 12). With KCN it turns into nitroso-cyanide, m.p. 171° (C. 1902, II. 363). **Pinene nitroso-bromide,** m.p. 92°. While aromatic bases, like aniline and methyl-aniline, reject NOCl, and regenerate pinene, it turns into nitrolamines with aliphatic bases: pinene-nitrolamine, m.p. 137° (C. 1907, I. 1040); pinene-nitrolpiperidide, m.p. 119°. By the action of sodium alcoholate, it splits off HCl and forms **nitroso-pinene** $C_{10}H_{14}$: NOH, m.p. 131°, which is regarded as the oxime of an unsaturated ketone, carvo-pinone, into which it turns, on heating with aqueous oxalic acid. By reduction with zinc dust and glacial acetic acid, it forms **pinylamine** $C_{10}H_{15}NH_2$; a ketone isomeric with camphor, **pino-camphone,** is also formed.

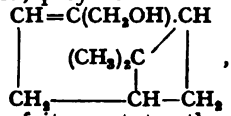
β-Pinene, *nopinene* (formula below), b.p. 162°–163°, D_{22} 0·866, n_D=1·4724, is found in small quantities beside α-pinene in turpentine oils, especially American, in a lævo-rotatory form. It has also been traced in lemon oil, coriander oil, hyssop oil, and the oil of Siberian pine needles (C. 1909, II. 2158). It has been synthesised from nopinol-acetic acid by heating with acetic anhydride (A. **363**, 9). It unites with HCl to form a mixture of bornyl chloride and dipentene dichlorohydrate; with nitrosyl chloride it does not, like α-pinene, form an addition product. But it unites with nitrous acid to a very unstable pseudo-nitrosite, which, on treatment with ammonia, or by distillation with steam (A. **346**, 243), turns into **nitro-terebentene,** nitro-β-pinene $C_{10}H_{15}NO_2$, with rejection of hyponitrous acid. The latter, on reduction with Sn and HCl, yields **amido-terebentene** $C_{10}H_{15}NH_2$, b.p.$_{12}$ 95°, from which, with nitrous acid, an alcohol is obtained, which, on oxidation with chromic acid, turns into tetrahydro-cumin-aldehyde, or cuminic acid (A. **346**, 246; cp. Phellandrene).

On oxidation with $KMnO_4$, we obtain from the **β-pinene-glycol** $C_{10}H_{16}(OH)_2$, m.p. 76°, which is first formed, **nopinic acid** $C_{10}H_{16}O_3$, m.p. 126°, an α-oxy-acid characterised by its sparingly soluble sodium salt, and a ketone, **nopinone** $C_9H_{14}O$ (A. **356**, 227; **368**, 9).



β-Pinene β-Pinene-glycol Nopinic acid Nopinone.

Alcohols. — *Univalent Alcohols.* — **Pino-carveol** $C_{10}H_{15}OH$, b.p. 215°–218°, probably contained in the oil of *Eucalyptus globulus* (A. **346**, 277). It is made artificially by the action of nitrous acid upon pinylamine (A. **346**, 221). On oxidation with chromic acid it yields pino-carvone, and on heating with potassium bisulphate, or dilute sulphuric acid, p-cymol.

Myrtenol  , b.p. 223°, D_{20} 0·9763, $[\alpha]_D$ +45° 45′, in the form of its acetate, the chief constituent of myrtle oil. The myrtenyl chloride $C_{10}H_{15}Cl$, formed by the action of PCl_5, yields, on reduction with Na and alcohol, d-α-pinene. On oxidation with chromic acid the corresponding aldehyde is obtained, myrtenal $C_{10}H_{14}O$, b.p.$_{10}$ 87°–90°. By means of $KMnO_4$ myrtenol can be reduced to d-pinic acid (B. **40**, 1363).

Methyl-nopinol, *pinene hydrate* $C_9H_{14}\langle^{OH}_{CH_3}$, m.p. 59°, b.p. 205°, smells of camphor, and is obtained from nopinone and CH_3MgI. By the action of dilute sulphuric acid, it passes into optically active α-terpineol (A. **360**, 88) and terpin hydrate. With glacial acetic acid and HCl, it turns into dipentene-dihalogenide. With PCl_5 it gives a chloride, b.p.$_{12}$ 97°–105°, which must be regarded as the true chlorohydrate of pinene (A. **356**, 239). **Ethyl-** and **propyl-nopinol,** see A. **360**, 91.

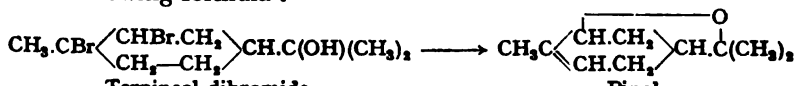
Pino-campheol $C_{10}H_{17}OH$, b.p. 218°, by reduction of pino-camphone. Its methyl-xanthogenate, m.p. 61°, yields, on heating, α-pinene (C. 1908, I. 1179).

Polyvalent Alcohols.—These no longer contain the carbon skeleton of pinene.

Pinol hydrate, *sobrerol* $C_{10}H_{16}(OH)_2$, is known in three modifications. **d-Pinol hydrate,** melting at 150°, $[\alpha]_D$ = + 150°, and **l-pinol hydrate,** melting at 150°, $[\alpha]_D$ = − 150°, are produced when dextro- and lævo-turpentine oil are oxidised in the air on exposure to sunlight. [d+l]-Pinol hydrate results on treating pinol with hydrobromic acid and alkali, as well as upon mixing equimolecular quantities of d- and l-pinol hydrates. Pinol hydrate is an unsaturated compound. Bromine converts it into a *dibromide*, melting at 131°. Potassium permanganate changes it to a tetra-acid alcohol, **sobrerythrite** $C_{10}H_{16}(OH)_4$, melting at 156° (B. **29**, 1195, R. 587).

An isomeric sobrerythrite, m.p. 194°, is obtained from the result of the action of ClOH upon pinene (B. **32**, 2069).

Pinol, [d+l]-sobrerone $C_{10}H_{16}O$, boiling at 183°, with sp. gr. 0·953 (20°), n_D=1·46949, is optically inactive. It is formed when the three pinol hydrates are treated with dilute sulphuric acid, and from the dibromide of terpineol by the splitting off of 2HBr. It is as indifferent as cineol towards hydroxylamine, phenyl-hydrazin, and acid chlorides. This, as well as its formation from terpineol dibromide, is represented in the following formula :



Terpineol dibromide — Pinol.

Pinol hydrate is a hydrate corresponding to this oxide, an oxy-terpineol, which results from pinene by the rupture of the pinene ring.

Pinol dibromide $C_{10}H_{16}Br_2O$, melting at 94° and boiling at 143° (11 mm.), is converted by sodium or alcoholic potash into pinol.

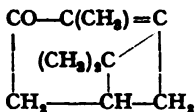
With HBr it gives pinol tribromide $C_{10}H_{17}Br_3O$. The latter splits off HBr, and forms an isomeric iso-pinol dibromide which, with potash, easily forms i-carvone and, on reduction, a new ketone, **pinolone** $C_{10}H_{16}O$ (A. **306**, 267).

Formic acid reduces it to cymene (A. **268**, 225). **Pinol nitroso-chloride** $C_{10}H_{16}O.NOCl$, melting at 103°, forms nitrolamines with bases. **Pinol-glycol** $C_{10}H_{16}O(OH)_2$, melting at 125°, is obtained from pinol dibromide with silver oxide or lead hydroxide, or from its *diacetate*, melting at 97° (A. **268**, 223). It is also formed from **pinol oxide** $C_{10}H_{16}O_2$, b.p. 207°, with dilute acids. The latter is obtained from the pinene-dichloro-hydrins with alkalies, and should be regarded as the dianhydride of sobrerythrite. A stereo-isomeric pinol-glycol is formed by the oxidation of pinol with $KMnO_4$ (B. **28**, 2710; C. 1898, II. 543).

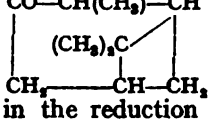
Pinol-chloro-hydrins $C_{10}H_{16}OCl(OH)$, m.p. 131°, are also obtained from the pinene-dichloro-hydrins, the dextro-form resulting from l-pinene and the lævo-form from d-pinene (B. **32**, 2070).

Bases.—Pinylamine $C_{10}H_{15}NH_2$, b.p. 207°, D 0·943, by reduction of nitroso-pinene (A. **268**, 197). By the action of nitrous acid it turns into pino-carveol. **Amido-terebentene** (see above).

Dihydro-pinylamine, *pino-camphylamine* $C_{10}H_{17}NH_2$, b.p. 199°, by reduction of nitroso-pinene with Na and amyl alcohol (C. 1907, I. 252).

Ketones. — Carvo-pinone  (?), b.p.$_{12}$ 95° (A. **346**, 231), is formed by heating nitroso-pinene, which may be regarded as carvo-pinone-oxime, with aqueous oxalic acid. Hydroxylamine regenerates nitroso-pinenes. Acids easily isomerise it to carvone. It is isomeric with—

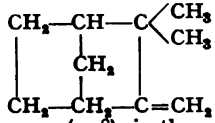
Pino-carvone $C_{10}H_{16}O$, b.p.$_{12}$ 95°, the oxidation product of pino-carveol. $KMnO_4$ decomposes it to form pinic acid (A. **346**, 222).

Pino-camphone  , b.p.$_{12}$ 87°, D 0·959, is formed beside pinylamine in the reduction of nitroso-pinene with zinc and glacial acetic acid. l-Pino-camphone has been found in the oil of *Hyssopus officinalis* (C. 1909, II. 2158). By oxidation with $KMnO_4$ it forms pinonic acid and a dicarboxylic acid isomeric with camphoric acid, $C_{10}H_{16}O_4$, m.p. 186° (A. **346**, 235).

Nopinone (constitution, see above), b.p. 209°, D_{20} 0·981, an oxidation product of β-pinene. On heating with dilute H_2SO_4, it is isomerised into Δ^2-iso-propyl-cyclo-hexenone (A. **356**, 227). The **nopinol-acetic acid** $C_9H_{14}(OH)CH_2COOH$, m.p. 84°, obtained by condensation with bromo-acetic ester and zinc (A. **368**, 7), forms the fundamental

material for the partial synthesis of α- and β-pinene as well as fenchene (*q.v.*).

IV. Camphane Group.

1. **Hydrocarbons.—Camphene**  (?), m.p. 48°–52°, b.p. 159°–161°, D_{54} 0·842, n_D=1·45514 (54°), is the only known natural *solid* terpene. It is known in a d-, l-, and an optically inactive modification; these are similar in chemical deportment. Camphene has been found, by a rearrangement, in iso-borneol, in the oil from *Andropogon nardus*, and in camphor oil (B. **27**, R. 163). It is obtained (1) from borneol by the action of potassium bisulphate at 200°; (2) by the action of $ZnCl_2$ or dilute sulphuric acid upon iso-borneol; (3) when sodium acetate and glacial acetic acid at 200° act upon pinene hydrochloride; and (4) on digesting bornyl chloride with aniline, pyridin, alkaline phenolates, etc. The so-called camphene hydrate, and synthetic methyl-camphenilol, turn into camphene with special ease, eliminating water.

Camphene only contains one double linking. Camphene and bromine in ether produce:

Camphene dibromide $C_{10}H_{16}Br_2$, melting at 89°, together with liquid **bromo-camphene** $C_{10}H_{15}Br$ (B. **29**, 544, 697, 900).

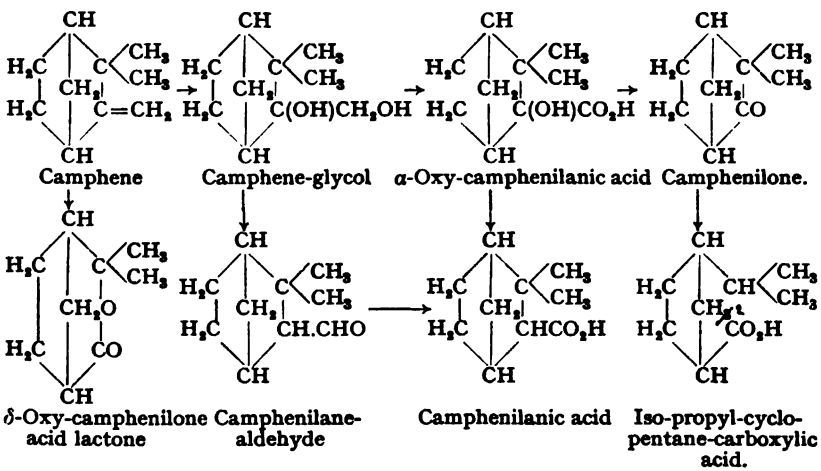
Camphene hydrochloride $C_{10}H_{17}Cl$, melting at 149°–151°, is produced when HCl is conducted into an alcoholic camphene solution. It is identical with the iso-bornyl chloride obtained from iso-borneol, and probably stereo-isomeric with pinene chlorohydrate, since both chlorides turn into the same camphene, on reduction with Na and alcohol, or by decomposition of their Mg compound with water. From pinene chlorohydrate, camphene chlorohydrate is specially distinguished by the greater ease with which it passes into camphene, under the influence of dehydrating agents. Camphene, treated with glacial acetic acid and concentrated sulphuric acid, yields *iso-borneol acetate*. The action of fuming nitric acid upon a chloroform solution of camphene leads to an additive product $C_{10}H_{16}(HNO_3)$, $b.p._{10}$ 110°, which regenerates camphene with alcoholic potash (C. 1900, II. 261).

Camphenile nitrite, *nitro-camphene* $C_8H_{14}>C:CHNO_2$, m.p. 66°, $b.p._{12}$ 147°, is found among the oxidation products of camphene volatilising in steam under the action of dilute nitric acid. It is also produced by the action of nitrous acid upon camphene (B. **32**, 1498), probably by splitting off hypo-nitrous acid from the very unstable pseudo-nitrosite formed at first. This, on reduction, yields camphenilane-aldehyde, and, by oxidation with $KMnO_4$ or the action of alcoholic potash, camphenilone; while, with concentrated H_2SO_4, it yields the completely saturated **tricyclene-carboxylic acid** $C_{10}H_{14}O_2$, m.p. 148°, which is indifferent to $KMnO_4$ (B. **41**, 2747; *Ch. Ztg.* **34**, 65).

On oxidising camphene with $KMnO_4$ (A. **340**, 17), **camphene-glycol** $C_{10}H_{16}(OH)_2$, m.p. 200°, is first formed, m.p. 200°; and this, treated

with dilute H_2SO_4, splits off water and turns into **camphenilane-aldehyde** $C_{10}H_{16}O$, melting at 70° and boiling at 96° (14 mm.). The oxidation of this aldehyde gives rise to two isomeric **camphenilanic acids** $C_{10}H_{16}O_2$, melting at 65° and 118°, which can be changed through the corresponding *α-bromo-acid* into *oxy-camphenilanic acid*, camphenilol acid, $C_{10}H_{16}O_3$, melting at 171°. This latter acid is also formed when camphene is oxidised with potassium permanganate. Its further oxidation causes the elimination of carbon dioxide and the formation of a ketone, **camphenilone** $C_{10}H_{14}O$, melting at 43° and boiling at 81° (12 mm.). This is the lower ring-homologue of camphor; it resembles the latter in odour and in chemical behaviour. By the oxidation of sodium amide, camphenilone is broken up to the amide of 2-iso-propyl-cyclo-pentane-carboxylic acid (B. **39**, 2580), which has been disintegrated into 2-iso-propyl-cyclo-pentanone (C. 1908, I. 1271), and has, on the other hand, been obtained synthetically from β-iso-propyl-adipinic acid (C. 1909, I. 443).

The ozonide produced on treating camphene with ozone, on decomposition with water, or glacial acetic acid, yields camphenilone and the lactone of **δ-oxy-camphenilonic acid** (B. **48**, 1432) with splitting of the camphene ring. This has also been obtained synthetically by the action of methyl-magnesium iodide upon the anhydride of cyclo-pentane-1, 3-dicarboxylic acid (B. **42**, 898). These various transformations are easily understood on the basis of G. Wagner's camphene formula :

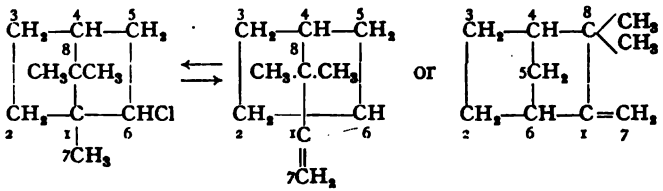


On oxidising the artificial and natural camphenes with $KMnO_4$ (but not with ozone) we obtain, besides the compound already mentioned, considerable quantities of a dicarboxylic acid, isomeric with camphene-camphoric acid $C_{10}H_{16}O_4$, m.p. 136° (inactive), 144° (active) (A. **375**, 336). Its genesis from the above camphene formula can hardly be imagined to take place without the supposition of considerable atomic displacement. It yields no anhydride, and no cyclic-ketone, in the distillation of its calcium salt. Its constitution, and its connec-

tion with the oxidation products of camphene, are not yet clear (A. **375**, 336). It is possible that it owes its origin to a hydrocarbon isomeric with the above camphene, which would indicate that camphene is a mixture of two isomeric terpenes (see also Tricyclene, below). But this can hardly be made to agree with the almost quantitative conversion of camphene into iso-borneol (see also A. **382**, 265; **383**, 1).

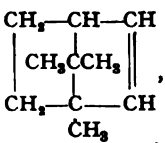
A primary transposition is, no doubt, the cause of the production of the tribasic **carboxyl-apo-camphoric acid**, camphoric acid $C_7H_{11}(COOH)_3$, m.p. 196°, in the oxidation of camphene with dilute nitric acid. With chromyl chloride in CS_2 solution, camphene yields an additive compound, $C_{10}H_{16}.2CrO_2Cl_2$, which is decomposed by water with formation of a camphenilane-aldehyde. In the animal body camphene is oxidised to camphenilane-aldehyde (C. 1903, I. 594). Oxidation with chromic acid converts camphene into camphor.

The above camphene formula therefore indicates that the preparation of camphene from the chlorohydrate of pinene or camphene, or from borneol and iso-borneol, is accompanied by a peculiar atomic displacement, which is reversed by the attachment of halogen hydride and other acids. This transposition involves the conversion of a five-membered ring into a six-membered ring, as shown in the following diagram:

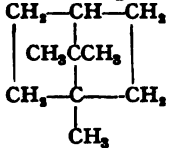


It is closely related to the atomic displacement occurring in the conversion of pinacolin alcohol or its chloride into tetramethyl-ethylene (Vol. I.).

Under special conditions it is possible to avoid the atomic displacement occurring during the elimination of water from borneol, or the elimination of halogen hydride from bornyl haloids, and thus to attain the hydrocarbon forming the foundation of these compounds:

Bornylene  , m.p. 113°, b.p. 146°, $[\alpha]_D$ −21·69°. It is remarkable on account of its great volatility. It is formed from bornyl iodide with concentrated alcoholic potash (C. 1910, I. 2089), or by the dry distillation of bornyl-xanthogenic methyl ester (C. 1905, I. 94), besides camphene, which can be separated by conversion into iso-bornyl acetate. It is obtained in a pure state from bornylene-carboxylic acid, by elimination of CO_2. Bornylene is oxidised by $KMnO_4$ to camphoric acid.

Camphane, 1, 7, 7-*trimethyl-nor-camphane, dihydro-bornylene*



, m.p. 153°, b.p. 159°, sublimes easily. It is formed by the reduction of camphene and pinene hydrochloride or hydro-iodide with sodium and alcohol, or by the decomposition of their magnesium compounds with water, besides small quantities of **hydro-dicamphene** $(C_{10}H_{17})_2$, m.p. 85°. As indicated by its symmetrical structure, it is always inactive, whether we start with active or inactive material (B. **39**, 1127). On heating with dilute nitric acid, it gives **nitro-camphane**, m.p. 125°–129°.

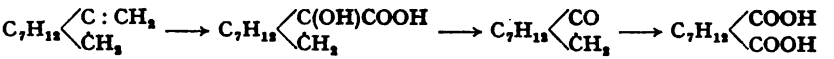
Iso-camphane, 5, 5, 6-*trimethyl-nor-camphane, dihydro-camphene* $C_{10}H_{18}$, m.p. 63°, is formed by the reduction of camphene with molecular hydrogen in the presence of platinum black (A. **382**, 265), and by heating iso-borneol with zinc dust to 220° (B. **33**, 774), in the latter case, no doubt, with intermediate formation of camphene.

Tricyclene $C_{10}H_{16}$, m.p. 68°, b.p. 153°, is completely saturated. It is contained in small quantities (about 0·4 per cent.) in crude camphene, and remains unchanged during its oxidation with $KMnO_4$ (A. **340**, 17). It is probably identical with the tricyclic hydrocarbon obtained by reduction with zinc dust and alcohol.

Fenchene $C_{10}H_{16}$ has not hitherto been traced with certainty in nature. It is formed from the fenchyl chlorides by heating with aniline, quinolin, or alcoholic potash, from iso-fenchyl alcohol by heating with zinc chloride, or by the action of nitrous acid upon fenchylamine. According to the nature of the foundation material, we can obtain dextro- or lævo-rotatory or inactive fenchenes, with boiling-points ranging from 154° to 158°, D about 0·87, and $n_D = 1{\cdot}4724$. Synthetically, a fenchene, either dextro- or lævo-rotatory according to the conditions, has been obtained from nopinol-acetic ester by splitting off water, and by the distillation of the resulting unsaturated acid (A. **363**, 1). Fenchene combines with bromine to form a crystalline dibromide, m.p. 62° (inactive), 88° (active). With halogen hydride it forms liquid monohalogen hydrates, apparently identical with fenchyl haloids. In the oxidation with permanganate, fenchene behaves very much like camphene. An α-oxy-acid, **oxy-fenchene acid** $C_{10}H_{16}O_3$, is produced first, and D-l- and L-d-fenchene* yield the two optical antipodes of this acid, m.p. 153°, $[\alpha]_D = \pm 63°$, while the less stable D-d-fenchene yields a feebly dextro-rotatory oxy-fenchenic acid, m.p. 138°. By oxidation of these acids we obtain ketones $C_9H_{14}O$, fencho-camphorones, m.p. 110° and 63°, lower homologues of camphor closely resembling it and yielding on further oxidation **apo-camphoric acid**, which is also easily obtained from fenchene with nitric acid (A. **302**, 371; **315**, 273; C. 1898, I. 575; 1899, II. 1052).

The gradual disintegration of fenchene is represented by the following series of formulæ :

* The capital letters D- and L- indicate the optical rotation of the d- or l-fenchones used in the preparation.

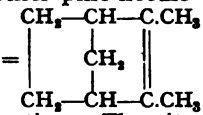


D-l-Fenchene — Oxy-fenchenic acid — Fencho-camphorone — Apocamphoric acid.

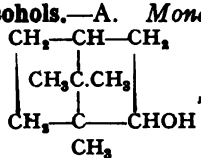
Since the formula of fenchone may be taken as clearly established, we must assume an atomic displacement in its conversion into fenchene corresponding to what happens in the conversion of camphor into camphene.

Tetrahydro-fenchene $C_{10}H_{20}$, b.p. 160°–165°, $D_{22} = 0{\cdot}7945$, $n_D = 1{\cdot}4370$, from fenchone and fenchyl alcohol by heating with HI.

Dihydro-fencholene C_9H_{18}, see Fencholenic acid.

In connection with camphene and fenchene, we may mention a hydrocarbon which, from its composition, C_9H_{14}, may be regarded as a lower homologue of terpene. It is found in Indian sandal-wood, in Siberian pine-needle oil, and other pine-needle oils (B. **40**, 4918), and has been termed **santene** C_9H_{14} =  , b.p. 140°, D_{20} 0·863, $n_D = 1{\cdot}46658$. It is optically inactive. The nitroso-chloride crystallises in blue needles to m.p. 109°, which, after a short time, become colourless. *Nitrosite*, m.p. 125°. *Monochlorohydrate*, m.p. 80°. *Tribromide* $C_9H_{13}Br_3$, m.p. 63°. During the oxidation with $KMnO_4$ we obtain, with intermediate formation of santene-glycol $C_9H_{14}(OH)_2$, m.p. 197°, a diketone $C_5H_8(COCH_3)_2$, b.p.$_9$ 124°–127°, which, on treating with alkaline bromine solution, turns into trans-cyclo-pentane-1, 3-dicarboxylic acid (B. **41**, 385).

A hydrocarbon, probably identical with santene, is formed by boiling the **teresantaric acid** $C_{10}H_{14}O_2$, m.p. 157°, also occurring in sandal-wood, with dilute sulphuric acid. By heating with formic acid, the teresantaric acid turns into an alcohol, the so-called **π-nor-borneol,** *santenol*, m.p. 98°, b.p.$_9$ 88°, which is also obtained from santene by hydration with formic acid or glacial acetic acid and sulphuric acid, and whose chloride, m.p. 60°, b.p.$_{10}$ 73°, on treatment with alcoholic potash, reverts into santene (B. **40**, 4465; **41**, 125).

2. **Alcohols.**—A. *Monacid Alcohols.*—**Borneo camphor, borneol,** *camphol*  , melting at 203° and boiling at 212°, occurs in three modifications in nature. d-Borneol is found in *Dryobalanops camphora*, a tree growing in Borneo and Sumatra, also in rosemary oil. *l-Borneol* and *inactive borneol* are present in the so-called baldrianic camphor. Many wood-spines contain it in the form of a fatty acid ester, more especially the acetic ester.

Borneol is very similar to Japan camphor, but has an odour at the same time resembling that of pepper. It sublimes very readily.

Artificially, it is formed, besides iso-borneol, by the reduction of camphor with sodium and alcohol (A. **280**, 225), and by the action of oxygen upon the magnesium compound of pinene chlorohydrate, which

must therefore be regarded as bornyl chloride (B. **39,** 1127). In the form of its ester, borneol is obtained by heating pinene with organic acids such as oxalic, benzoic, salicylic, chloro- and nitro-benzoic acids, etc. (C. 1906, II. 1589; 1909, I. 1025). On oxidation, it turns into camphor without change in the direction of optical rotation. On heating with potassium bisulphate or zinc chloride it splits up, though with some difficulty, into water and camphene.

Methyl ether, b.p. 194°. *Ethyl ether*, b.p. 204° (B. **24,** 3713). *Acetyl ester*, m.p. 29°, *rhombic hemihedral*, $b.p._{10}$ 98°, $n_D=1{\cdot}46635$, $[\alpha]_D=+38°\ 20'$, also found in oil from Siberian fir (C. 1903, I. 515).

The bornyl haloids are identical with the so-called pinene hydrohaloids. Bornyl iodide, on treating with alcoholic potash, yields *bornylene*. **Bornyl-iso-valerianate**, b.p. 255°–260°, occurs in baldrian oil, and is used in pharmacy under the name "*bornyval*." Bornyl salicylate ("*salite*") is used as an anti-neuralgic.

d- and **l-Bornyl-xanthogenic methyl esters** $C_{10}H_{16}OCS.SCH_3$ yield d- and l-bornylene on distillation at ordinary pressures.

Iso-borneol $C_{10}H_{17}OH$, m.p. 212°, is probably the stereo-isomeric alcohol corresponding to borneol. It is more volatile than borneol, and is formed together with the latter in the reduction of camphor, into which it passes by oxidation with $KMnO_4$, ozone, etc., with reversal of its optical rotation (B. **39,** 1131). By the action of sodium in xylol or benzine solution, iso-borneol is transformed into borneol (C. 1909, II. 25). Iso-bornyl acetate, $b.p._{13}$ 107°, is formed by heating camphene with glacial acetic acid and 50 per cent. H_2SO_4 to 50°–60° (German patent 67,255; B. **27,** R. 102), or by transformation of pinene chlorohydrate with Zn acetate and glacial acetic acid, in which case the zinc chloride acts catalytically (C. 1907, II. 434). Both reactions are of industrial importance as regards the artificial production of camphor from pinene. Both borneol and iso-borneol are formed by the action of oxygen upon magnesium-camphene chlorohydrate (B. **39,** 1135). With dehydrating agents it passes into camphene much more easily than borneol.

Camphene hydrate $C_{10}H_{11}O_8$, m.p. 150°, b.p. 205°, is formed on digesting camphene chlorohydrate with milk of lime. It smells both of fungus and menthol, and passes easily into camphene, on shaking up with dilute mineral acids, and sometimes on mere distillation (B. **41,** 1092; A. **383,** 1).

Methyl-camphenilol $C_{10}H_{17}OH$, m.p. 118°, b.p. 205°, has been obtained by the action of CH_3MgI upon camphenilone. On heating with glacial acetic acid and H_2SO_4 it splits off water and easily passes into camphene (A. **340,** 58).

Camphol alcohol $C_{10}H_{19}OH$, m.p. 60°, b.p. 213°, is formed by the reduction of campholic ester with sodium and alcohol (C. 1904, II. 303). It differs from the tertiary alcohol of the same name, b.p. 203°, produced by the action of silver nitrite upon campholamine chlorohydrate (B. **27,** R. 126). This indicates that, in this case, a change in the ring system has taken place (cp. A. **379,** 202).

Camphel alcohol $C_9H_{17}OH$, melting at 25° and boiling at 179°, results from the interaction of camphelamine hydrochloride and silver nitrite. It is a tertiary alcohol. It readily decomposes into water and the hydrocarbon C_9H_{16} (B. **27,** R. 126).

Camphenilol $C_9H_{15}OH$, m.p. 84°, by reduction of camphenilone with sodium and alcohol (A. **366,** 72).

Fenchyl alcohol $C_{10}H_{17}.OH$, melting at 45° and boiling at 201°, with specific gravity 0·933, is produced in two modifications: by the reduction of d- and l-fenchone. It has a penetrating and very disagreeable odour. L-d-fenchyl alcohol, $[\alpha]_D = +10° 36'$, is obtained from l-fenchone and l-fenchyl alcohol, $[\alpha]_D = -10° 35'$, from d-fenchone (A. **284,** 331).

i-Fenchyl alcohol has been found in the yellow pine oil of *Pinus palustris*. It is also formed, besides other alcohols, in the hydration of β-pinene (C. 1909, II. 25). On oxidation it yields fenchone besides oxy-dihydro-fencholenic acid (B. **42,** 2698), and, on splitting off water, fenchene.

Fenchyl chlorides $C_{10}H_{17}Cl$, $b.p._{14}$ 84°–86°, are formed from fenchyl alcohol with PCl_5 or HCl, and from fenchene with chlorine hydride. Fenchyl chlorides, of various origins, show different optical rotatory powers, and are probably mixtures of isomeric (secondary and tertiary ?) chlorides. **l-Fenchyl bromide** $C_{10}H_{17}Br$, $b.p._{14}$ 90°–100° (*J. pr. Ch.* **2, 62,** 1). **D-l-Fenchyl acetate,** $b.p._{10}$ 88°.

Iso-fenchyl alcohol, m.p. 62°, $b.p._{13}$ 98°. Like iso-borneol, its acetate is formed from fenchene with acetic-sulphuric acid. While fenchyl alcohol yields fenchone upon oxidation, iso-fenchyl alcohol produces an isomeric ketone, iso-fenchone.

Iso-fencholene alcohol $C_{10}H_{17}OH$, b.p. 218°, with specific gravity 0·927 (20°), $n_D = 1·476$, is produced when alcohol and sodium act upon fencholene amide (A. **284,** 337). It is readily attacked by potassium permanganate. When heated with dilute sulphuric acid it changes to **fenchenol** $C_{10}H_{18}O$, b.p. 183°, with specific gravity 0·925 (20°), $n_D = 1·46108$. This compound, with the exception of the boiling-point, cannot be distinguished from cineol.

Thio-borneol $C_{10}H_{17}SH$, m.p. 63°, $b.p._{12}$ 95°, by the action of sulphur upon bornyl-magnesium chloride, and through transposition of hydro-pinene-sulphinic acid, camphane-sulphinic acid $C_{10}H_{17}SO_2H$, m.p. 64°, obtained from bornyl-magnesium chloride and SO_2. Chromic acid oxidises thio-borneol into bornyl disulphide $(C_{10}H_{17})_2S_2$, m.p. 178°, which, on distillation at ordinary pressure, decomposes into thio-borneol and thio-camphor (B. **39,** 3503).

3. **Amines** have been obtained by the reduction of nitroso-pinenes, oximes, and nitriles, as well as ketones with ammonium formate.

Bornylamine $C_{10}H_{17}.NH_2$ melts at 159° and boils at 199°. The formyl compound is produced when camphor is heated with ammonium formate, and the base itself by the reduction of camphor-oxime with alcohol and sodium.

In the latter reaction two geometrically isomeric optically active bases are obtained: bornylamine, m.p. 173°, $[\alpha]_D = +45·5°$; and neo-bornylamine, m.p. 180°, $[\alpha]_D = -31·3°$ (C. 1898, II. 300).

Bornylamine possesses an odour like that of camphor and piperidin (A. **269,** 347). Heated with acetic anhydride, it splits up at 200°–210°, forming camphene (A. **269,** 347).

Camphylamine $C_9H_{15}.CH_2.NH_2$, boiling at 194°–196°, is produced when the nitrile of campholenic acid is reduced. The *benzoyl compound* melts at 77° (B. **20,** 485; **21,** 1128).

Campholamine $C_{10}H_{19}.NH_2$, and **camphelamine** $C_9H_{17}NH_2$, see Campholic acid.

Camphenamine $C_8H_{14}\langle^{CNH_2}_{CH}$, b.p.$_{200}$ 161°, D_{20} 0·9399, formed from chloro-camphenamine with soda, which is obtained from amido-borneol $C_{10}H_{16}(OH)(NH_2)$, the reduction product of amido-camphor (B. **33**, 481). With HNO_2, camphenamine gives a tertiary unsaturated alcohol $C_{10}H_{15}(OH)$, m.p. 102°, the so-called *β*-iso-camphor, isomeric with camphor and closely resembling it (A. **318**, 59).

Camphenylamine $C_9H_{15}.NH_2$, m.p. 91°, b.p. 185°, by reduction of camphenilone-oxime with Na and alcohol (A. **366**, 75).

Camphane-diamine $C_{10}H_{16}(NH_2)_2$, a wax-like mass, b.p. 246°, formed by reduction of camphor-dioxime or amido-camphor-oxime (C. 1905, II. 178).

Fenchylamine and fencholenamine sustain the same relation to each other that we observed in bornylamine and camphylamine.

Fenchylamine $C_{10}H_{17}NH_2$, boiling at 195°, with specific gravity 0·9095 (22°), is known in three modifications, produced from the corresponding fenchones on heating them with ammonium carbonate, or by reducing the fenchone-oximes. **D-l-Fenchylamine**, $[\alpha]_D = -24·89°$, obtained from d-fenchone, yields D-l-fenchene and d-limonene on the action of HNO_2. The optical rotatory power of a series of derivatives has been studied :

Formyl-, acetyl-, propionyl-, butyryl-fenchylamines, $[\alpha]_D = -36·56°$, $-46·62°$, $-53·16°$, $53·11°$ (A. **276**, 317).

Fencholenamine $C_9H_{15}.CH_2.NH_2$, boiling at 110°–115° (21–24 mm.), results from the reduction of the nitrile of fencholenic acid nitrile (A. **268**, 138).

Fenchelylamine $C_9H_{17}NH_2$, b.p. 173°, is formed from fenchelyl isocyanate $C_9H_{17}N : CO$, the result of the action of potassium hypobromite upon fencholic acid amide. On dry distillation its chlorohydrate yields apo-fenchene C_9H_{16}, b.p. 143°, D_{21} 0·7945 (A. **369**, 79 ; C. 1910, II. 875).

4. **Ketones.**—Various transformation products of the ketones $C_{10}H_{16}O$, *camphor* and *fenchene*, have been treated in the preceding sections. By reduction they yield *borneol* and *fenchyl alcohol*, from which they are conversely again obtained by oxidation.

Camphor is known in two optically active modifications and one optically inactive modification, while fenchone is known in two optically active forms.

d-Camphor, *common camphor*, *Japan camphor* $C_{10}H_{16}O_2$, melting at 175° and boiling at 204°, with $[\alpha]_D = +44·22°$ in alcohol (A. **250**, 352), is found in the camphor tree (*Cinnamomum camphora*). It is obtained by distillation with steam and sublimation. Artificially, it is made on an industrial scale by changing oil of turpentine (pinene) into borneol or iso-borneol, and oxidising with $KMnO_4$, ozone, nitric acid, etc., but the result is mostly inactive. Camphor is also formed by oxidation of camphene with chromic acid. It is a colourless, transparent mass, crystallises from alcohol, and sublimes in shining prisms of specific gravity 0·985. It is very volatile, and is applied therapeutically as well as in the manufacture of celluloid and smokeless powder. Its alcoholic solution is dextro-rotatory. Camphor yields pure cymol if

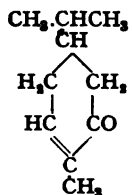
distilled with P_2O_5, and on boiling with iodine forms carvacrol $C_{10}H_{14}O$. When boiled with nitric acid it yields different acids, chiefly camphonic and camphoronic acids. Upon reduction it passes into borneol and iso-borneol.

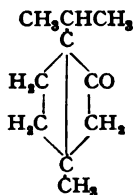
l-Camphor, matricaria camphor, is contained in the oil of *Matricaria Parthenium*. It resembles d-camphor even to the rotatory power $[\alpha]_D = -44{\cdot}22°$. It yields l-camphoric acid upon oxidation.

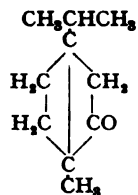
(d+l)-Camphor, melting at 178·6°, is produced on mixing d- and l-camphors, and by the oxidation of i-borneol and i-camphene with chromic acid (B. **12,** 1756). Also by racemising ordinary camphor with $AlCl_3$ (C. 1899, I. 1243).

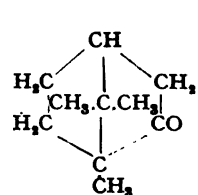
Constitution of Camphor.—The camphor formula (1) proposed by Kekulé (1873) satisfactorily accounted for the change of camphor into p-cymol and carvacrol. However, the ready anhydride formation of camphoric acid, which had led to a seven-membered ring, could not be brought by it into accord with the known experiences relating to the anhydride formation of aliphatic dicarboxylic acids. The lack of additive power also remained unexplained. The formulæ of Kanonnikoff and Bredt explained these relations much better. In them the p-carbon atoms of the hexagon of camphor were brought in direct union. The anhydride formation of camphoric acid, thus made parallel with ethylene-succinic acid, could be understood on the basis of this formula. Baeyer (1893) showed that, as camphoric anhydride melted higher than its hydrate, it probably contained an n-glutaric acid anhydride ring (A. **276,** 265).

Camphoric acid is not the only oxidation product of camphor, for when it is further oxidised camphanic acid and camphoronic acid are produced. In the latter acid J. Bredt recognised α, α, β-trimethyl-tricarballylic acid, inasmuch as it decomposed, upon the application of heat, into trimethyl-succinic anhydride, iso-butyric acid, carbonic acid, water, and carbon; whereas, when camphoronic acid, the lactone of oxy-camphoronic acid, obtained from it, is fused with caustic potash, trimethyl-succinic acid and oxalic acid are produced very readily. Bredt concludes from this behaviour that the carbon grouping of camphoronic acid, as well as that of trimethyl-succinic acid, must be present in camphanic acid, camphoric acid, and camphor. The formula of Bredt (1893) may be imagined (B. **26,** 3047) to have been evolved from that of Kekulé by rotating the iso-propyl group about 180°, until it lies within the hexagon, and then its middle carbon atom is allowed to unite the two p-carbon atoms of the hexagon by the migration of an H atom and the dissolution of the double union :


(Kekulé, 1873)

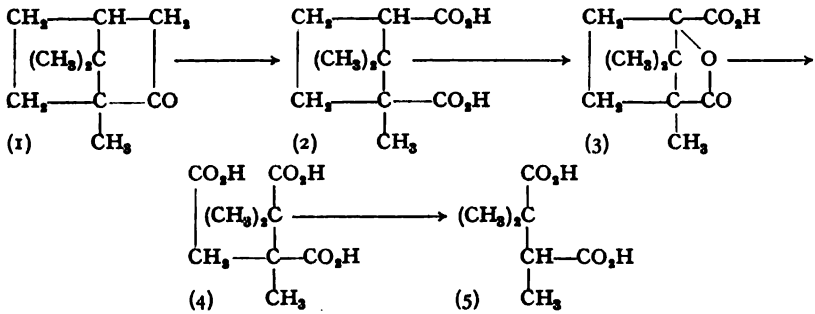

(Kanonnikoff, 1883)


(Bredt, 1884)


(Bredt, 1893).

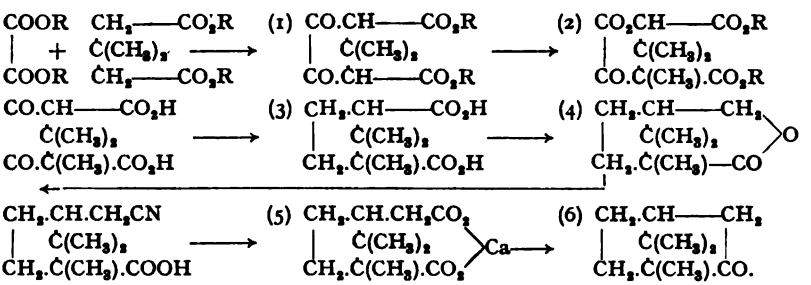
The position of the CO group is proved by the conversion of camphor into carvacrol (see above).

The oxidation of camphor (1) to camphoric acid (2), camphanic acid (3), and camphoronic acid (4), as well as the decomposition of the latter into trimethyl-succinic acid (5), also found among the oxidation products of camphor (B. **26**, 2337), is represented in the following diagram :—



This interpretation is corroborated by the *synthesis of camphor*, which can be carried out as follows (Komppa, A. **370**, 209).

Oxalic ester and β-dimethyl-glutaric acid ester are condensed by sodium ethylate to diketo-apo-camphoric acid ester (1) ; by means of methylation with methyl iodide and sodium, in alcoholic solution, this is turned into diketo-camphoric acid ester (2). By means of the intermediate products—dioxy-, dehydro-, and bromo-camphoric acid—the diketo-camphoric acid may be reduced to a mixture of cis- and trans-[d+l]-camphoric acid (3), which are separated by utilising their different behaviour in forming anhydrides. cis-Camphoric anhydride is reduced to the lactone campholide (4) by means of Na amalgam, and this combines with potassium cyanide to the nitrile of homo-camphoric acid (5). The latter, which can also be prepared from cyano-camphor by saponification and splitting, yields camphor (6) on distillation of its calcium salt :



Since racemic camphoric acid can be split up into d- and l-camphoric acids by means of its cinchonidin salt, the above process is also useful for the preparation of optically active camphor.

On a second method of synthesising camphor, see Perkin and Thorpe, C. 1906, II. 241.

On the stereo-isomerism of the camphor molecule, see A. **316**, 196 (also J. Bredt, *Über die räcemliche Configuration des Camphers*, Leipzig, 1905).

The camphor formula leads to the formulæ for borneol, camphene, and numerous other compounds in genetic connection with camphor. The recognition of the connection between camphor and its transformation products is frequently impeded by far-reaching molecular rearrangements undergone by these bodies, especially with acid reagents (cp. β-campholenic acid, β-campholytic acid, etc.).

Transformation Products of Camphor.—Chlorine and bromine convert camphor into mono- and di-substitution products. α- and β, d-**chloro-camphor** melt at 92° and 100°. α- and β-**Dichloro-camphor** melt at 93° and 77°, while α- and β-**bromo-camphor** melt at 76° and 61°. On the action of sodium upon bromo-camphor, dicamphor $(C_{10}H_{15}O)_2$, and dicamphene-dione $(C_{10}H_{14}O)_2$, see C. 1898, I. 295, and B. **37,** 1569. With magnesium in ether the α-bromo-camphor yields bromo-magnesium-camphor, which is found to be very suitable for syntheses (B. **36,** 2608; **37,** 749). α- and β-**Dibromo-camphor,** m.p. 61° and 115° (cp. C. 1897, II. 76); on the decomposition of α-dibromo-camphor, see C. 1900, I. 198. α-**Iodo-camphor,** m.p. 43°, is formed by the saponification of iodo-formyl-camphor, or by the action of iodine upon sodium-camphor. α-**Di-iodo-camphor,** m.p. 109°, is formed by the action of iodine upon alkaline alcoholic solution of formyl-camphor (B. **37,** 2156).

With PCl_5 camphor gives several **camphor dichlorides,** *dichloro-camphanes* $C_8H_{14}\begin{cases}CH_2\\|\\CCl_2\end{cases}$ which, on shaking up with concentrated sulphuric acid, split the bridge linkage, and pass easily into carvenone.

By heating camphor with alcoholic ammonium sulphide, a mixture of sulphides is obtained which, on distillation, yields **thio-camphor** $C_{10}H_{16}S$, red crystals, m.p. 119°, b.p.$_{15}$ 104°, and thio-borneol (B. **36,** 863).

By heating chloro-camphor and bromo-camphor with nitric acid, or by chlorinating or brominating nitro-camphor, we obtain **chloro-** and **bromo-nitro-camphor,** which, on reduction with copper zinc, or on treatment with sodium methylate, give **nitro-camphor** (B. **22,** R. 266; **23,** R. 115; **29,** R. 270; **37,** 2077; C. 1899, I. 1078). By reduction, nitro-camphor yields amido-camphor. An isomeric nitro-camphor $C_8H_{14}\langle^{CNO_2}_{C(OH)}$ (?), m.p. 70°, is formed from iso-nitroso-camphor by oxidation with nitric acid (C. 1902, II. 897).

Camphor-sulphonic acids and their transformation products, see B. **28,** R. 643; **29,** R. 512; C. 1898, I. 619; 1902, II. 1464; 1903, I. 923. The d-camphor-sulphonic acid, and especially the d-bromo-sulpho-camphoric acid, are often useful for splitting up racemic bases.

Camphor-oxime $C_{10}H_{16}:NOH$, m.p. 118°, b.p. 249° (A. **259,** 331), gives, on reduction, bornylamine. Potassium hypobromite converts it into **bromo-nitro-camphane** $C_8H_{14}\langle^{CH_2}_{CBr(NO)_2}$, m.p. 220°, which, on reduction, gives **nitro-camphane** $C_{10}H_{17}NO_2$, m.p. 148° (C. 1900, I. 544). By the action of nitrous acid upon camphor-oxime we obtain the nitrate of **α-camphorimine** $C_8H_{14}\langle^{CH_2}_{C:NH}$ (?), m.p. about 95°, isomeric with β-camphorimine and camphenamine, besides a substance $C_{16}H_{16}N_2O_2$, m.p. 43°, which is termed *pernitroso-camphor* or *camphenile*

nitramine, isomeric with camphor dioximes, and converted by sulphuric acid into a ketone isomeric with camphor (B. **29**, 2807; C. 1905, II. 623). Camphor-oxime and **camphor-phenyl-hydrazone**, b.p. 210°, can also be easily prepared from thio-camphor (B. **36**, 868).

β-Camphor, *bornylone* $C_8H_{14}\langle^{CO}_{CH_2}$, m.p. 185°, b.p. 214°, structurally isomeric with camphor, is formed by the action of acids upon **β-camphorimine** $C_8H_{14}\langle^{C:NH}_{CH_2}$, obtained from the azide of bornylene-carboxylic acid by Curtius' transposition. In small quantities it is also obtained from α-oxy-camphane-5-carboxylic acid by oxidation with CrO_3 (*Ch. Ztg.* **35**, 765).

Camphor-quinone $C_8H_{14}\langle^{CO}_{CO}$, m.p. 198°, is formed from iso-nitroso-camphor by boiling with dilute sulphuric acid, upon the action of nitrous acid or sodium bisulphite, or by the action of campho-carboxylic acid (B. **27**, 1447). It resembles the quinone of the α-diketones, has a peculiar sweet odour, is volatile with steam, and sublimes at 50°–60° in golden-yellow needles (A. **274**, 71). Camphor-quinone easily passes into camphoric acid derivatives, under the influence of various reagents (cp. B. **30**, 657, 659). Concentrated sulphuric acid converts it into a ketonic acid $C_{10}H_{16}O_3$; fuming sulphuric acid produces a transposition of camphor-quinone even at 0°, with splitting up of the $CH_3.C.CH_2$ bridge, and enolisation of a keto-group (B. **35**, 3829).

Iso-nitroso-camphor $C_8H_{14}\langle^{C:N\,OH}_{C:O}$ exists in two forms, melting at 153° and 114° respectively (C. 1908, I. 1270); it is formed by the action of amyl nitrite and sodium ethylate upon camphor. Concentrated sulphuric acid converts it into camphoric acid imide (B. **26**, 241). Acetyl chloride, PCl_5, or soda and acetic anhydride produce camphoric acid mononitrile (B. **29**, R. 651). Zinc and dilute acids produce amido-camphor (A. **274**, 71). **Camphor-quinone-phenyl-hydrazone** $C_8H_{14}\langle^{C:NNHC_6H_5}_{CO}$, m.p. 155°, is produced, besides its *desmotropic form* $C_8H_{14}\langle^{C.N:NC_6H_5}_{C(OH)}$, m.p. 180°, by the action of diazo-benzol chloride upon campho-carboxylic acid (B. **32**, 1995; cp. C. 1902, II. 210).

bis-Camphanonaxine, *azo-camphenone* $C_8H_{14}\langle^{C:N.N:C}_{CO\quad\;OC}\rangle C_8H_{14}$, m.p. 222°, is obtained from camphor-quinone with hydrazin, and from azo-camphor by heating, together with camphenone (B. **27**, R. 892; C. 1897, II. 761).

Camphor-dioxime, α-dioxime, m.p. 201°, **β-dioxime**, m.p. 248°, are formed from iso-nitroso-camphor with acetic hydroxylamine. **γ-Dioxime**, m.p. 135°, from iso-nitroso-camphor with free hydroxylamine, on melting, passes into *δ-dioxime*, m.p. 199°. The dioximes are distinguished by their optical rotatory power (C. 1903, I. 1352). By reduction they yield the peroxide $C_{10}H_{16}N_2O_2$, m.p. 144°. They are also produced from bromo-pernitroso-camphor, a bromination product of pernitroso-camphor with hydroxylamine (C. 1900, II. 574).

α-Oxy-camphor $C_8H_{14}\langle^{CHOH}_{CO}$, m.p. 203°–205°, is formed from camphor-quinone by reduction with glacial acetic acid and zinc dust.

It is easily alkylated and acylated. Sodium amalgam reduces it to camphor. Sodium and alcohol, to **camphor-glycol** $C_8H_{14}\langle^{CHOH}_{CHOH}$, m.p. 231°. This camphor-glycol is isomeric with the camphene-glycol obtained from camphene with $KMnO_4$, and must be regarded as the glycol of bornylene. By oxidation of oxy-camphor, camphor-quinone is regenerated (B. **35**, 3811).

Campherol $C_{10}H_{16}O_2$, m.p. 197°–198°, is apparently isomeric with α-oxy-camphor. It occurs in the form of a glucuronic acid compound in the urine of dogs fed with camphor (B. **30**, 660).

Amido-camphor $C_8H_{14}\langle^{CH.NH_2}_{CO}$, b.p. 244°, from nitro-camphor, or, better, from iso-nitroso-camphor, by reduction. It is a mass resembling paraffin, and smelling of fish. It condenses on standing to **dihydro-camphene-pyrazin** $C_8H_{14}\langle^{CH—N=C}_{C=N—CH}\rangle C_8H_{14}$, m.p. 116°, and, as an α-amido-ketone, it is suitable for hetero-ring formations (cp. A. **313**, 25). **Amido-camphor-chlorohydrate,** m.p. 224°, acts like curare, but much more feebly. Acetyl compound, m.p. 122°. **Camphoryl-glycocoll ester** $C_{10}H_{15}O.NHCH_2CO_2C_2H_5$ is poisonous (A. **307**, 207; B. **31**, 3260; **32**, 1538; **35**, 3657). **Camphoryl-carbamide** $C_8H_{14}\langle^{CH.NHCONH_2}_{CO}$, m.p. 169°, from amido-camphor and potassium cyanate, yields, with nitrous acid, **camphoryl-iso-cyanate** $C_{10}H_{15}O.N:C:O$, m.p. 77°, a substance very prone to reaction, from which numerous counter-derivatives have been obtained.

Camphoryl-mustard oil $C_{10}H_{15}O.N:C:S$, m.p. 106·5° (C. 1908, I. 257).

Azo-camphor, *monoketazo-camphor-quinone* $C_8H_{14}\langle^{C\langle^{N}_{N}}_{CO}$, m.p. 74°, yellow crystals, is obtained by the action of nitrous acid upon amido-camphor-chlorohydrate (B. **26**, 1718); with potassium sulphite it gives hydrazin sulphonate, which is split up by concentrated HCl into hydrazin and camphor-quinone (B. **29**, R. 1115).

Camphenone $C_8H_{12}\langle^{CH}_{CO}$(?), m.p. 168°–170°, is formed besides azo-camphenone by heating azo-camphor. It smells of camphor. **Oxime,** m.p. 132° (B. **27**, R. 590). For the action of bromine and HBr upon camphenone, see B. **29**, R. 1108.

If we wish to attach carbon groups to the camphor amalgam, sodium camphor $(C_{10}H_{15}O)Na$, obtained from camphor with sodium and sodium amide, is particularly suitable, and so is camphor-magnesium bromide $(C_{10}H_{15}O)MgBr$, obtained from α-bromo-camphor with magnesium in ether, in benzene, toluol, etc. By the action of halogen alkyl CO_2, cyanogen, carboxylic esters, chlorides or anhydrides, of aldehydes and ketones upon these bodies, the radicles $-CH_3$, $-CO_2H$, -CN, -COR, -CH(OH)R', -C(OH)RR', =CHR are introduced instead of the hydrogens of the $-CH_2$ -CO group in camphor. The resulting products are capable of many transformations.

d-Campho-carboxylic acid $C_8H_{14}\langle^{CHCO_2H}_{CO}$, m.p. 128°, with evolution of CO_2. It is formed from camphor with sodium, or, better, from

sodium amide and CO_2 in benzene, or from bromo-camphor Mg and CO_2 in ether (B. **36,** 668, 1305). The acid and its esters: **methyl ester,** b.p.$_{15}$ 155°–160°; **ethyl ester,** b.p.$_{21}$ 167°, give green and blue colorations respectively, with ferric chloride. With sodium and alkyline iodide the esters yield alkyl-campho-carboxylic ester: **methyl-campho-carboxylic methyl ester** $C_8H_{14}\langle^{C(CH_3)CO_2CH_3}_{CO}$, m.p. 87° (acid: m.p. 104°), **ethyl-campho-carboxylic ethyl ester,** b.p.$_{15}$ 165°. Some of these esters are difficult to saponify. With carboxylic haloids the sodium campho-carboxylic esters change into O-acylated products $C_8H_{14}\langle^{CCO_2R}_{COAc}$; but with benzol-sulpho-chloride besides benzol-sulphinic acid, α-chloro-campho-carboxylic ester is formed. **α-Bromo-** and **α-iodo-campho-carboxylic esters** $C_8H_{14}\langle^{CXCO_2R}_{CO}$ are easily obtained (B. **36,** 1732). With phenyl-hydrazin and campho-carboxylic ester, two isomeric campho-phenyl-pyrazalones are obtained (B. **32,** 1987).

By electrolytic reduction of campho-carboxylic acid in alkaline solution we obtain **cis-** and **trans-borneol-carboxylic acid** $C_8H_{14}\langle^{CHCOOH}_{CHOH}$, m.p. 101° and 171° respectively. $KMnO_4$ oxidises only the cis-acid of camphoric acid, whereas nitric acid oxidises both. With acetyl chloride both give rise to the aceto-compounds of the trans-acid, m.p. 123°. By elimination of water both acids, but the cis-acid more readily, turn into **bornylene-carboxylic acid** $C_8H_{14}\langle^{CCOOH}_{CH}$, m.p. 113°, b.p.$_{13}$ 158°. The latter unites with HCl or HBr in glacial acetic acid to form β-chloro- and β-bromo-hydro-bornylene-carboxylic acid, m.p. 85° and 91°, the alkaline salts of which, on boiling in aqueous solution, yield bornylene besides other products, and yield it in a particularly pure form. By reduction of β-bromo-hydro-bornylene-carboxylic acid with potassium amalgam, or of bornylene-carboxylic acid with hydrogen and palladium, we obtain:

Camphane-5-carboxylic acid $C_8H_{14}\langle^{CHCO_2H}_{CH_2}$, m.p. 91°, which is geometrically isomeric with the acid obtained by the action of CO_2 upon bornyl-magnesium chloride.

Camphane-6-carboxylic acid, *hydro-pinene-carboxylic acid* $C_8H_{14}\langle^{CH_2}_{CHCOOH}$, m.p. 73° (A. **366,** 1; B. **38,** 3799).

The nitrile of campho-carboxylic acid, **cyano-camphor** $C_8H_{14}\langle^{CHCN}_{CO}$, m.p. 127°, is formed from sodium camphor with gaseous cyanogen, and also from oxy-methylene camphor, by heating with hydroxyl-amine chlorohydrate, which also produces its oxime (A. **281,** 349). From sodium cyano-camphor, with alkylene iodide, we simultaneously obtain **O-** and **C-alkyl-cyano-camphor** $C_8H_{14}\langle^{C.CN}_{COAlk}$ and $C_8H_{14}\langle^{C(Alk)CN}_{CO}$ (C. 1903, I. 1085); from the latter, by saponification and elimination of CO_2, we obtain the alkyl camphor **methyl-camphor** $C_8H_{14}\langle^{CH.CH_3}_{CO}$, m.p. 38°, $[\alpha]_D$+27°, which, with bromine, produces *methyl-bromo-camphor,* which, in turn, on treatment with alcoholic potash, yields **methylene-camphor** $C_{10}H_{14}O : CH_2$, m.p. 30°–35°, b.p. 218°, $[\alpha]_D$+127°

(C. 1903, I. 971). **Ethyl-camphor,** b.p. 226°–229°, $[\alpha]_D$+40°, yields after the same treatment **ethylidene-camphor** ($C_{10}H_{14}O$) : $CHCH_3$, b.p.$_{10}$ 110°–115°, $[\alpha]_D$+113° (C. 1904, I. 948).

Dimethyl-camphor $C_8H_{14}\langle^{C(CH_3)_2}_{CO}$, b.p.$_{11}$ 106°, a mobile liquid smelling at the same time of camphor and menthone. It is formed by the action of sodium amide and methyl iodide upon camphor in ether or benzene solution; by heating with $NaNH_2$ it is split up to form the amide of dimethyl-campholic acid, m.p. 74° (C. 1909, II. 442; cp. Fenchone).

Oxy-methylene-camphor, *formyl-camphor* $C_8H_{14}\langle^{C:CHOH}_{CO}$, m.p. 80°, b.p.$_{28}$ 138°, is formed from sodium-camphor or camphor-magnesium bromide and formic ester, as well as by the action of sodium methylate free from alcohol upon α-monohalogen and dihalogen camphor (B. **37,** 2069); the oxy-methylene-camphor is a strong acid: **methyl ether** ($C_{10}H_{14}O$) : $CHOCH_3$, m.p. 40°, b.p. 262°; **acetate** ($C_{10}H_{14}O$) : $CHOCOCH_3$, m.p. 63°, b.p. 290°–293°; with PCl_5, **chloro-methylene-camphor** ($C_{10}H_{14}O$) : CHCl, b.p.$_{16}$ 119° is generated; with bromine and iodine in neutral solution we obtain bromo- and iodo-formyl-camphor, m.p. 41° and 68° respectively. With nascent prussic acid we obtain the cyano-hydrin $(C_{10}H_{15}O)CH\langle^{OH}_{CN}$, m.p. 122°, which, on boiling with acetic anhydride, yields **cyano-methylene-camphor** ($C_{10}H_{14}O$) : CHCN, m.p. 46°, b.p. 280°, the nitrile of **camphor-methylene-carboxylic acid** ($C_{10}H_{14}O$) : $CHCO_2H$, m.p. 101° (A. **281,** 306).

By reduction of the formyl-camphors with sodium and alcohol we obtain two stereo-isomeric **camphyl-glycols** $C_8H_{14}\langle^{CH.CH_2OH}_{CHOH}$, **cis-glycol,** m.p. 87°, **trans-glycol,** m.p. 118°. $KMnO_4$ oxidises the trans-glycol into trans-borneol-carboxylic acid, while the cis-glycol—probably with intermediate formation of the cis-borneol-carboxylic acid, which is attacked by $KMnO_4$, yields camphoric acid (A. **366,** 62).

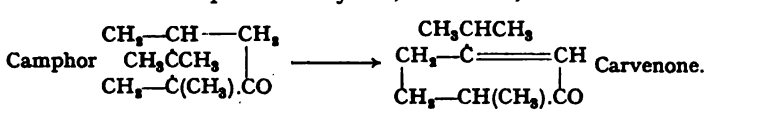
The homologous acyl-camphors $C_8H_{14}\langle^{C:C(OH)R}_{CO}$ (desmotropic forms: $C_8H_{14}\langle^{CH.COR}_{CO}$ and $C_8H_{14}\langle^{C.COR}_{COH}$), is obtained from camphor-magnesium bromide with fatty-acid esters, chlorides, and anhydrides, in which case dicamphonyl-alkyl-carbinols $(C_{10}H_{15}O)_2C(OH)Alk$ occur as intermediate products (B. **36,** 2663; **37,** 762); or by the action of alkyl-magnesium compounds upon cyano-camphor (C. 1906, I. 1468). **Acetyl-, propionyl-, butyryl-, i-valeryl-camphor,** b.p.$_{11}$ 118°, 129°, 132°, 141°–148°. **Benzoyl-camphor,** two forms, m.p. 87°–88°, m.p. 89° respectively, is also formed from sodium camphor with benzoyl chloride in toluol (C. 1903, I. 233, 458).

By the condensation of camphor-magnesium bromide, with aldehydes and ketones in ether, we obtain secondary and tertiary alcohols, some of which split off water: **camphoryl-methyl-carbinol** $(C_{10}H_{15}O)CH(OH)CH_3$, b.p. 223°–226°, is formed from camphor-magnesium bromide with acetaldehyde in small quantities, together with acetyl-camphor. From benzaldehyde and camphor-magnesium bromide we only obtain benzoyl-camphor. From sodium-camphor and benzaldehyde we obtain **benzylidene-camphor** $(C_{10}H_{14}O)CHC_6H_5$, m.p. 96°, which is also formed

by reduction of benzoyl-camphor, and which, on further reduction, yields benzyl-camphor $(C_{10}H_{15}O)CH_2C_6H_5$, m.p. 128°, and is split up by heating with HBr to **benzylidene-campholic acid** $C_8H_{14}\langle^{CH:CHC_6H_5}_{COOH}$; their aromatic aldehydes condense, like benzaldehydes, with sodium-camphor (C. 1901, II. 418). From $(C_{10}H_{15}O)MgBr$ with acetone we obtain **camphoryl-dimethyl-carbinol** $(C_{10}H_{15}O)C(OH)(CH_3)_2$, m.p. 88°, b.p. 210°–215°, which, on boiling with dilute sulphuric acid, yields **iso-propylidene-camphor** $(C_{10}H_{14}O):C(CH_3)_2$, b.p. 200°–204°; **camphoryl-diphenyl-carbinol** $(C_{10}H_{15}O).C(OH)(C_6H_5)_2$, m.p. 122°, from $(C_{10}H_{15}O)MgBr$ with benzo-phenone (B. **36,** 2627).

With oxalic ester and sodium ethylate, camphor condenses to **camphor-oxalic acid** $C_8H_{14}\langle^{CH.COCOOH}_{CO}$, m.p. 88°, from which a number of derivatives have been prepared (C. 1900, I. 905; 1901, II. 544; 1908, I. 1182).

Broken Ring-products of Camphor.—The splitting up of the camphor-ring system can take place in two ways in its first phase. In one way the bridge group CH_3CCH_3 of camphor, which is always in a strong state of strain, "rises up." On the other hand, the splitting may take place at the keto-group of camphor, in which case derivatives of the 5-membered camphoceane-ring contained in camphor are formed (A. **299,** 162). Examples of the former kind are shown by the transformations of camphor into cymol, carvacrol, and carvenone:



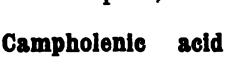
An analogous reaction is the transformation of camphor-quinone by fuming sulphuric acid (cp. the splitting up of carone and pinene, above.)

The second group of disintegrations comprises the transformations of camphor into campholic acid, campholenic acid, and camphoric acid.

(*a*) **Campholic acid** $C_8H_{14}{}^{CH_3}_{COOH}$, m.p. 107° (active), m.p. 109° (inactive), is formed by heating camphor-borneol or iso-borneol with caustic potash to 250°–280° (B. **28,** R. 376; C. 1909, I. 1562). By boiling with nitric acid it is oxidised to camphor-camphoric acid and camphoronic acid (B. **27,** R. 752); on the other hand, campholic acid can be recovered from camphoric acid by reducing camphoric anhydride to α-campholide, converting the latter with HBr into bromo-campholic acid and heating this with zinc dust to 50°–60° (C. 1900, I. 603). **Anhydride,** m.p. 58° (inactive), m.p. 66° (inactive). **Chloride,** b.p. 222°, decomposes on heating with P_2O_5 into HCl, CO, and campholene. The amide melts at 79° (active) and 90° (inactive).

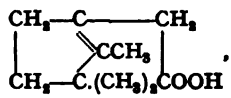
The **nitrile** melts at 72° and boils at 218°. It yields *campholamine,* $C_{10}H_{19}NH_2$, melting at 210°, upon reduction. Bromine and caustic alkali change the amide to *camphelyl-iso-cyanate,* boiling at 201°, from which *camphelamine* $C_9N_{17}NH_2$, melting at 43° and boiling at 175°, is obtained (B. **26,** R. 21; **27,** R. 126). **Iso-campholic acid,** B. **29,** R. 356. The camphor-ring in camphor-oxime can be very easily ruptured

by mineral acids, the products being α- and β-campholene-nitrile, iso-amino-camphor, and dihydro-campholene-lactone.

α-Campholenic acid  boils at 256°. Its specific gravity equals 0·992 (19°). It is optically active, $n_D = 1{\cdot}47125$. The *nitrile*, b.p. 226°, of this acid is produced with water exit when dilute sulphuric acid or acetyl chloride acts upon camphor-oxime. The reduction of the nitrile produces **α-camphylamine** $C_{10}H_{17}NH_2$, boiling at 195°. Alcoholic potash saponifies it to *α-campholamide*, melting at 130°, which with alkali hypobromite gives the lower homologue of camphylamine, **α-amido-campholene** $C_9H_{15}NH_2$, b.p. 185° (C. 1899, II. 385), and on further saponification campholenic acid. The latter is oxidised by potassium permanganate to :

α-Dioxy-hydro-campholenic acid $C_9H_{15}(OH)_2CO_2H$, melting at 144°, and a ketonic acid, **l-pinonic acid,** which affords decomposition products similar to those of the like-named oxidation product of pinene. Chromic acid oxidises α-campholene- or dihydro-dioxy-campholenic acid to **iso-keto-camphoric acid** $C_{10}H_{16}O_5 = CH_3.CO.C(CH_3)_2CH(CH_2COOH)_2$, and, eventually, to **iso-camphoronic acid** $CO_2H.C(CH_3)_2CH(CH_2COOH)_2$ (A. **289**, 19 ; C. 1899, II. 833), m.p. 167°. Concentrated sulphuric acid, when warmed with the latter body, sets free CO, and terpenylic acid results (B. **29**, 3006).

Campholenic acid is stable in the presence of alkalies, but acids transpose it in a peculiar manner (*Ch. Ztg.* 1900, 858) into



β-campholenic acid, melting at 52° and boiling at 245°, which is optically inactive. Its *nitrile*, boiling at 220°–230°, is produced in the action of stronger acids (concentrated HI) upon camphor-oxime. It is reduced to **β-camphylamine,** melting at 197°, which may be saponified to an *amide*, melting at 86°. Potassium permanganate oxidises β-campholenic acid to a dihydroxy-acid, melting at 146°, and with it an oily acid which readily changes to *iso-camphorone* $C_9H_{14}O$, boiling at 217°. Chromic acid oxidises the β-acid to **γ-acetyl-iso-capronic acid** $CH_3.CO.C(CH_3)_2CH_2CH_2COOH$, melting at 48°. Further oxidation leads to a decomposition into α-dimethyl-glutaric acid and α-dimethyl-succinic acid. The same decomposition products are obtained from iso-camphorone (B. **30**, 242). The conversion of β-campholenic acid, when heated with bromine, into 1, 3, 4-xylyl-acetic acid (B. **29**, R. 643) is peculiar.

β-Dihydro-campholene-lactone, melting at 30° and boiling at 256°, appears as the principal or the by-product in the decompositions of camphor-oxime by strong acids, and may be obtained by acids from the two campholenic acids, as well as from iso-amino-camphor.

Synthetically, it is prepared by the action of CH_3MgI upon 3, 3-*dimethyl-cyclo-pentanone-acetic ester* (C. 1908, I. 1056).

Chromic acid oxidises it to oxy-dihydro-campholene-lactone, melting at 144° (B. **30**, 404).

Iso-amino-camphor $C_{10}H_{17}ON$, boiling at 254°, is formed along with the preceding bodies when stronger acids act upon camphor-oxime, campholene-amides, and nitriles. It apparently contains a primary amine group, and is very similar to the isomeric amido-camphor. It changes quite readily to dihydro-campholeno-lactone (B. **30**, 324).

α-Dihydro-campholenic acid $C_{10}H_{18}O_2$, b.p.$_{22}$ 160°; the nitrile, b.p. 225°–228°, of this acid is obtained by heating the isomeric camphor-imine with access of air (B. **33**, 1929). By bromination, and elimination of HBr, we obtain the isomeric acid (C_8H_{14}) : CHCOOH, m.p. 70°, isomeric with campholenic acid, and this becomes 2, 3, 3-trimethyl-cyclo-pentanone, m.p. 165°, on oxidation with $KMnO_4$ (C. 1902, I. 585).

Campholene $\begin{matrix} CH_2—C(CH_3) \\ | \\ CH_2—C(CH_3)_2 \end{matrix}\!\!>\!CCH_2$ (?), boiling at 134°, is produced when α- or, better, β-campholenic acid has been heated. Carbon dioxide is eliminated. It is, further, formed from campholic acid or campholic acid chloride, when acted upon with P_2O_5. Synthetically, it has been obtained by the action of CH_3MgI upon 1, 1, 4-trimethyl-cyclo-pentanone-5, and elimination of water from the resulting tetra-methyl-cyclo-pentanol (C. 1907, II. 2050). It is optically inactive, and yields on oxidation **ββ-dimethyl-lævulinic acid** $CH_3COC(CH_3)_2CH_2COOH$, and unsym. dimethyl-succinic acid.

Campholene dibromide melts at 97°. Campholene, heated with HI acid to 280°, becomes hexahydro-pseudo-cumol, just as β-campholenic acid changes to xylyl-acetic acid (B. **30**, 594), and camphoric acid to tetrahydro-iso-xylol (B. **26**, 3053).

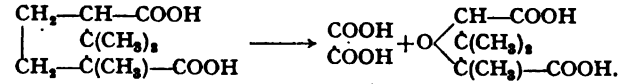
An apparently isomeric **campholene** C_9H_{16}, boiling at 137°, has been obtained together with carvacrol from chloro-camphor by the action of zinc chloride (B. **26**, R. 492).

Camphoric Acid.—There are four optically active, and two optically inactive, camphoric acids.

d-Camphoric acid, *ordinary camphoric acid* $\begin{matrix} CH_2—CH—COOH \\ C(CH_3)_2 \\ CH_2—C(CH_3)—COOH \end{matrix}$, m.p. 187°, $[\alpha]_D = +49{\cdot}7$ in alcohol, is obtained by heating d-camphor, or campholic acid, with nitric acid (A. **168**, 323), and, because it can be made without great trouble, has been exhaustively studied. When it is heated above the melting-point, or when it is treated with acetyl chloride (A. **226**, 1), it changes to its **anhydride,** melting at 221° and boiling at 270°. Synthesis of camphor, see above.

By fusion with caustic potash, camphoric acid changes to iso-propyl-succinic acid and l-iso-camphoric acid; by oxidation with nitric acid, camphoronic acid and dinitro-capronic acid $\begin{matrix} (CH_3)_2C.CO_2H \\ | \\ CH_3.C(NO_2)_2 \end{matrix}$ are produced, while with chromic acid the products are camphoronic and trimethyl-succinic acids. Water and bromine change it to camphanic acid (B. **28**, 2151). On oxidising camphoric acid with permanganate, we obtain, besides oxalic acid as a characteristic product, a dibasic acid $C_8H_{12}O_5$, m.p. 121°, which can be divided into optical antipodes. On reduction with HI, it yields αββ-trimethyl-glutaric

acid, and the anhydride of $\alpha\beta\beta$-trimethyl-glutaric acid, resembling ethylene oxide. Its formula and formation may be represented as follows :—



The distillation of calcium camphorate yields **camphorone** $CH_3—C[:C(CH_3)_2]\rangle CO$, $CH_2——CH(CH_3)\rangle$ b.p.$_{10}$ 83° (B. **26,** 3053). In this reaction there is not only a cyclic ketone formation, but an " erection " of the camphor bridge $CH_2.C.CH_3$. The constitution of camphorone, first deduced from the oxidation products, is confirmed by its synthesis from 2-methyl-cyclo-pentanone and acetone, with sodium ethylate (C. 1900, I. 604), and its breaking up into these components, on heating with caustic potash (A. **331,** 322), as well as its behaviour towards hydroxylamine, with which it gives an addition product, **camphorone-hydroxylamine** $C_9H_{15}O(NHOH)$, m.p. 120° (B. **32,** 1343). By reduction with sodium and alcohol we obtain a secondary alcohol, **dihydro-camphorol** $C_9H_{17}.OH$, and from this, with CrO_3, we obtain **dihydro-camphorone** $C_9H_{16}O$, b.p. 184°–185° (B. **37,** 236), identical with dihydro-pulegenone, and obtained synthetically from α-methyl-α_1-iso-propyl-adipinic acid (C. 1908, I. 1056).

Tetrahydro- and hexahydro-isoxylol are produced when camphoric acid is heated with hydriodic acid.

The d-camphoric acid forms two series of acid esters : the **α-esters,** produced by the partial saponification of the neutral esters, and the **β-esters,** resulting from the partial esterification of the acids (B. **26,** 289). For derivatives of ester acids, see C. 1906, I. 35.

The **dichloride** $C_8H_{14}\langle{}^{CCl_2}_{CO}\rangle O$ boils at 140° (15 mm.) (B. **23,** R. 229).

The **diamide** $C_8H_{14}C_2O_2(NH_2)_2$, melting at 197°, is converted by potassium hypobromite into $C_{10}H_{16}N_2O_2$, melting at 235°. This is probably the ureïde of an oxy-acid (B. **27,** R. 894), corresponding to campho-lactone. Two isomeric **camphor-amido-acids,** α-, m.p. 177°, and β-, 180°, have been obtained from the anhydride with ammonia, and from iso-nitroso-camphor with HCl (B. **29,** R. 96). The β-acid has been obtained from camphor-imide, with sodium hydroxide (B. **29,** R. 96 ; C. 1904, II. 1222). See below for decomposition products of these acids.

The **imide** $C_8H_{14}C_2O_2NH$, melting at 248° and boiling at 300°, is also formed from iso-nitroso-camphor (B. **26,** 58, 242 ; A. **257,** 308 ; **328,** 342), and from camphoric anhydride by distillation in a current of NH_3. In sulphuric acid solution, camphoric acid imide is reduced at lead electrodes to two isomeric lactames, **camphidonene** $C_8H_{14}\langle{}^{CH_2}_{CO}\rangle NH$, α-form, m.p. 231°, b.p. 295°, β-form, m.p. 228°, b.p. 308°, and further to the base **camphidin** $C_8H_{14}(CH_2)_2NH$, m.p. 186°, b.p. 209° (B. **34,** 3274). α- and β-Camphidone are also formed by heating the chlorohydrates of α- and β-amido-campholic acids (see below), the lactames of which are probably the camphidones (B. **40,** 4311).

Nitroso-α-camphidone, on heating with alkali, passes into α-

campholide (B. **38**, 3806). **Thio-camphoric acid imide** $C_8H_{14}(CS)_2NH$, m.p. 135° (C. 1910, I. 1253).

The **methyl imide** $C_8H_{14}\langle{}^{CO}_{CO}\rangle NCH_3$, m.p. 40°–42°, is obtained from silver camphoron-imide and methyl iodide, as well as by heating *methyl iso-imide* above its melting-point (B. **29**, R. 96).

Methyl iso-imide $C_8H_{14}\langle{}^{C=N.CH_3}_{CO>O}$, melting at 134°, results when camphor-methyl-amino-acid is treated with acetyl chloride or PCl_5 (B. **26**, R. 688).

Camphoryl-hydroxylamine $C_8H_{14}\langle{}^{CO}_{CO}\rangle N.OH$ melts at 225° (B. **27**, R. 893). It seems to be identical with so-called camphor nitro-phenol, obtained by boiling nitro-camphor in HCl (C. 1899, I. 111).

α-Camphor-nitrilic acid, *cyano-lauronic acid* $C_8H_{14}(CN)COOH$, melting at 152°, is formed when camphor-amino-acid is treated with acetyl chloride and subsequently with ammonia, or by the interaction of acetic anhydride or PCl_5 and iso-nitroso-camphor (B. **29**, R. 651, 779).

β-Camphor-nitrilic acid, m.p. 110°–113°, from β-camphor-amido-acid. On distillation of their calcium salts *both* isomeric acids break the ring, and yield the nitrile of dimethyl-heptenic acid $(CH_3)_2C:CH.CH_2.CH_2.CH(CH_3)CN$, b.p.$_{14}$ 89°–90°, which is also produced by the distillation of camphoric acid imide, and camphor-amido-acids with lime, and represents the lower homologue of citronellic acid nitrile (A. **328**, 338). By reduction with sodium and alcohol, α- and β-camphor-nitrilic acid are reduced to α- and β-amido-campholic acid $C_8H_{14}(CH_2NH_2)COOH$. Their chlorohydrates, α-, m.p. 248°, β-, m.p. 215°–222°, on heating turn into α- and β-camphidone (B. **40**, 4311).

l-Camphoric acid results from the oxidation of matricaria camphor. It resembles the d-variety in every particular, except the rotatory power.

[d+l]-Camphoric acid, *paracamphoric acid*, melting at 204°, is formed upon mixing alcoholic solutions of equimolecular quantities of d- and l-camphoric acids (B. **23**, R. 229).

d-Iso-camphoric acid, *d-cis-trans-camphoric acid*, melting at 171°, with $[\alpha]_D = +48°$, may be prepared by heating l-camphoric acid with water, or, better, with a mixture of glacial acetic acid and hydrochloric acid, which produces some dextro "iso-camphoric" acid. It does not form a real anhydride, hence can be easily separated by means of acetyl chloride from the l-camphoric acid.

l-Iso-camphoric acid, $[\alpha]_D = -48°$, is obtained from both d-camphoric acid and its chloride.

[d+l]-Iso-camphoric acid, melting at 191°, results from the union of d- and l-iso-camphoric acids. When they are heated the corresponding camphoric anhydrides are produced (B. **27**, 2001). Cp. B. **29**, 1700, for the crystal forms of the camphoric acids.

Camphanic acid $\begin{matrix} CH_3—C(CO_2H).O \\ | \quad CH_2CCH_3 \quad | \\ CH_3—C(CH_3)—CO \end{matrix}$, melting at 201°, is obtained on boiling bromo-camphoric anhydride with water. Nitric and chromic acids oxidise it to camphoronic acid. By distillation cam-

phanic acid loses carbon dioxide, and becomes campho-lactone and lauronolic acid (A. **227**, 1). Cp. B. **29**, R. 772, 861, for additional bromo- and oxy-camphoric acids.

On the breaking up of camphanic acid nitrile to camphononic acid, a 2, 2, 3-trimethyl-cyclo-pentanone-3-carboxylic acid, see C. 1901, II. 1308.

Dehydro-camphoric acid $\begin{matrix}CH{=}C.CO_2H\\ |\\ CH_2CCH_2\\ |\\ CH_2{-}C(CH_3)CO_2H\end{matrix}$, m.p. 202°–203°, is obtained by heating chloro- and bromo-camphoric acid ester with quinolin or diethyl-aniline, and subsequent saponification. It does not itself form an anhydride, but, on distillation, it shifts the double link, and passes into the anhydride of iso-dehydro-camphoric acid (acid, m.p. 178°–179°; anhydride, m.p. 182°–183°). Lauronolic acid (see below) is also produced, with elimination of CO_2 (B. **35**, 1286).

On treating the two camphor-amido-acids with bromine and alkali, two isomeric amino-acids are produced: α-camphor-amido-acid yields **amino-dihydro-lauronolic acid**, and β-camphor-amido-acid, **amino-dihydro-α-campholytic acid**:

$$\begin{matrix}CH_2{-}CH.CONH_2\\ |\quad\quad >C(CH_3)_2\\ CH_2.C(CH_3).COOH\end{matrix} \longrightarrow \begin{matrix}CH_2{-}CH.NH_2\\ |\quad\quad >C(CH_3)_2\\ CH_2.C(CH_3)COOH\end{matrix} \qquad \begin{matrix}CH_2{-}CH.COOH\\ |\quad\quad >C(CH_3)_2\\ CH_2.C(CH_3).CONH_2\end{matrix} \longrightarrow \begin{matrix}CH_2{-}CH.COOH\\ |\quad\quad >C(CH_3)_2.\\ CH_2.C(CH_3).NH_2\end{matrix}$$

Amino-dihydro-lauronolic acid (also called *amino-lauronic acid*), treated with acetic anhydride, gives a **lactame** $C_8H_{14}\begin{matrix}NH\\ CO\end{matrix}$, the nitroso-compound of which, on boiling with potash, forms some compounds which include the corresponding lactone, **dihydro-lauro-lactone** $C_8H_{14}\begin{matrix}O\\ |\\ CO\end{matrix}$, m.p. 32° (B. **35**, 1291; C. 1909, I. 1095). The amino-dihydro-α-campholytic acid, which can also be formed from camphoric acid chlorimide, with sodium alcoholate, also yields a lactame and, in the same way, a lactone $C_8H_{14}\begin{matrix}CO\\ O\end{matrix}$, **dihydro-campholyto-lactone**, m.p. 116° (A. **314**, 392).

Lauronolic acid $\begin{matrix}CH{=}{=}CH\\ |\quad\quad >C(CH_3)_2\\ CH_2{-}C(CH_3){-}COOH\end{matrix}$ (also called *γ-lauronolic acid* or *allo-campholytic acid*) is formed from amino-dihydro-lauronolic acid with nitrous acid, and from dehydro-camphoric acid, by splitting off CO_2. By oxidation in $KMnO_4$ or nitric acid, and splitting at the double link, it yields camphoronic acid (see below).

Iso-lauronolic acid $\begin{matrix}CH_2{-}C.CH_3\\ |\quad\quad C.CH_3\\ CH_2{-}C(CH_3)CO_2H\end{matrix}$ (?) (Woringer's *lauronolic acid*) is formed from camphanic acid by distillation, and from bromo-camphoric anhydride with soda. On boiling with HCl, lauronolic acid and iso-lauronolic acid give the same γ-lactone, **iso-dihydro-lauro-lactone** (formerly called *campho-lactone*) $C_8H_{14}\begin{matrix}O\\ |\\ CO\end{matrix}$, m.p. 50°, isomeric with the dihydro-lauro-lactone (B. **35**, 1290; *J. pr. Ch.* 2, **83**, 400).

α-Campholytic acid $\begin{matrix}CH_2—CH—COOH\\ |\quad\quad\quad\quad\\ CH=C(CH_3)\end{matrix}\!\!>C(CH_3)_2$, liquid, b.p.$_{15}$ 140°, is formed in the action of nitrous acid upon dihydro-amino-campholytic acid (see above) (besides **oxy-dihydro-campholytic acid** $C_8H_{14}(OH)COOH$, m.p. 132°, and its lactone, m.p. 116°), and by electrolysis of the potassium salt of α-camphor-methyl-ester acid. By oxidation with nitric acid, α-campholytic acid is oxidised to **dimethyl-tricarballylic acid** $COOH.C(CH_3)_2.CH(COOH).CH_2COOH$ (B. **33**, 2935). By dilute sulphuric acid it is transposed, like α- into β-campholenic acid (see above), into **β-campholytic acid** $\begin{matrix}CH_2—C—CO_2H\\ |\quad\quad\quad\\ CH_2—C:(CH_3)_2\end{matrix}\!\!>CCH_3$, m.p. 134° (formerly called *iso-lauronolic acid*). It is formed out of camphoric anhydride by the action of $AlCl_3$ (cp. C. 1900, I. 545; 1901, I. 78); it is also obtained by heating sulpho-camphylic acid to 200°. On heating with concentrated sulphuric acid, sulpho-camphylic acid is regenerated from β-campholytic acid. The β-campholytic acid contains no unsym. C atom, and is therefore optically inactive. On oxidation with chromic acid it yields, like β-campholenic acid, **dimethyl-hexanonic** or **acetyl-capronic acid** $CH_3COC(CH_3)_2CH_2CH_2COOH$ and **α-dimethyl-glutaric acid** (*A. Ch. Phys.* 7, **18**, 181; C. 1899, II. 871; cp. A. **314**, 392).

On a synthesis of α- and β-campholytic acid from 1, 1-dimethyl-butane-1, 2, 4-tricarboxylic acid, see C. 1903, I. 923. On the disintegration of dihydro-α- and -β-campholytic acid to 2, 2, 3- and 2, 3, 3-trimethyl-cyclo-pentanone, see C. 1902, II. 265; 1903, II. 287.

Iso-laurolene $\begin{matrix}CH_2—CH\\ |\quad\quad\\ CH_2—C:(CH_3)_2\end{matrix}\!\!>CCH_2$, b.p. 108°, is formed on heating iso-lauronolic acid to 300°. Synthetically, it has been obtained by the action of CH_3MgI upon 2, 2-dimethyl-cyclo-pentanone, and elimination of water from the resulting alcohol. With $KMnO_4$, dimethyl-hexanonic acid is formed, as in the case of β-campholytic acid. With acetyl chloride and $AlCl_3$, it yields, like the aromatic hydrocarbons, a ketone isomeric with camphor: **β-campholyto-methyl-ketone** $C_8H_{13}(COCH_3)$, b.p. 202°, also obtained from the chloride of β-campholytic acid, with zinc methyl and potassium hypobromite (C. 1909, I. 751).

Laurolene $\begin{matrix}CH_2—C(CH_3)=\\ CH_2—CH(CH_3)\end{matrix}\!\!>CCH_2$ (?), b.p. 121°, is formed by heating camphanic acid with water to 180°, and from the nitroso-compound of amino-laurolonic acid lactame, by boiling with soda (C. 1909, II. 801).

Sulpho-camphylic acid, *sulpho-camphoric acid* $C_8H_{12}\!\!<\!\!\begin{matrix}COOH\\ SO_3H\end{matrix} + 3H_2O$, melting at 160°–165°, is produced in the action of sulphuric acid upon camphoric acid. Upon heating it changes to β-campholytic acid; on fusing with soda, two acids are formed, $C_9H_{12}O_2$, α- and **β-camphylic acid,** m.p. 148° and 106° respectively. The former is reduced by sodium amalgam to inactive α-campholytic acid (see above, and C. 1902, II. 366; 1903, II. 571). On oxidising sulpho-camphylic acid with permanganate at 0°, it changes into the so-called camphorylic acid

$C_{18}H_{30}O_6$, a diketo-carboxylic acid (C. 1899, I. 931), and upon oxidation with nitric acid it yields sulpho-iso-propyl-succinic acid and dimethyl-malonic acid (B. **26**, 2044).

α-Campholide $\begin{matrix}CH_2—CH—CH_2\\ |\quad C(CH_3)_2\quad\rangle O\\ CH_2—C(CH_3).CO\end{matrix}$, melting at 211°, is formed in the reduction of camphoric anhydride with alcohol and sodium, just as phthalide is obtained from phthalic anhydride (B. **29**, R. 221, 288). Also by heating nitroso-α-camphidone with alkali, and by oxidising camphor with Caro's acid (B. **32**, 3630). With PCl_5 the lactone gives **chloro-campholic acid chloride** $C_8H_4(CH_2Cl)COCl$, m.p. 21°, b.p.$_{15}$ 132°; by treatment with HBr, **bromo-campholic acid** $C_8H_{14}(CH_2Br)COOH$, m.p. 177° with decomposition, which, by reduction, passes into campholic acid, and, with PCl_5, into **bromo-campholic acid chloride**, m.p. 37°, b.p.$_{15}$ 147°; **β-campholide** $C_8H_{14}\langle\begin{matrix}CO\\CH_2\end{matrix}\rangle O$, m.p. 219°, is formed in small quantity by reduction of camphoric acid β-methyl ester with Na and alcohol (C. 1906, I. 35; cp. B. **40**, 4311). Dialkyl-α-campholides, like dimethyl- and diethyl-α-campholide, b.p.$_{10}$ 146° and m.p. 38°, are obtained by the action of alkyl-magnesium haloids upon camphoric acid ester, or camphoric anhydride. In the latter case there are by-products in the shape of the corresponding campholides: dimethyl-β-campholide, m.p. 84° (C. 1910, II. 467).

Carboxyl-apo-camphoric acid, *campho-acid* $\begin{matrix}CH_2—CH—COOH\\ |\qquad\quad\rangle C(CH_3)_2\\ CH_2—C=COOH\\ \qquad\quad|\\ \qquad COOH\end{matrix}$, melting at 196°–200°, is produced in the oxidation of camphene with dilute nitric acid. It forms an *anhydride acid* when it is heated. This melts at 205°. It subsequently splits off CO_2 and passes into the anhydride of:

Apo-camphoric acid, *campho-pyro-acid* $\begin{matrix}CH_2—CH—COOH\\ |\qquad\quad\rangle C(CH_3)_2\\ CH_2—CH—COOH\end{matrix}$, melting at 204°, which is also formed by oxidising fenchene with nitric acid. It is synthesised by a series of suitable reductions from diketo-apo-camphoric acid (cp. synthesis of camphor) and obtained in a cis- and a trans- form (m.p. 204° and 190° respectively). The anhydride of the former melts at 175° (A. **368**, 126). In accordance with its symmetrical formula, apo-camphoric acid is optically inactive.

d-Camphoryl-malonic acid ester $C_8H_{14}\langle\begin{matrix}C=C(CO_2C_2H_5)_2\\ \rangle O\\ CO\end{matrix}$, m.p. 82°, b.p.$_{40}$ 247°, by the action of Na-malonic ester upon camphoric acid chloride (A. **257**, 298). Similar compounds are obtained by the transformation of chloro- and bromo-campholic acid chloride with Na-malonic methyl ester, which gives, besides halogen esters $C_8H_{14}\langle\begin{matrix}CH_2Hlg\\ COCH(CO_2CH_3)_2\end{matrix}$, m.p. 56° and 73°, an ester free from halogens $C_8H_{14}\langle\begin{matrix}CH_2\\ CO\end{matrix}\rangle C(CO_2CH_3)_2$ (?), m.p. 79° (R. Anschütz). Otherwise it behaves analogously to camphoric acid (B. **29**, R. 175, 773; *Ch. Ztg.*, 1896, p. 840).

d-Homo-camphoric acid, *hydroxy-campho-carboxylic acid*

$C_8H_{14}\langle^{CH_2.COOH}_{CO_2H}$, melting at 234°, is produced when cyano-camphor is boiled with aqueous caustic potash. Its *mononitrile* is formed on heating campholide with potassium cyanide (B. **29,** R. 288). d-Camphor is obtained on heating calcium homo-camphorate in a current of carbon dioxide.

d-Hydro-camphoryl-acetic acid $C_8H_{14}\langle^{CH_2.CH_2.CO_2H}_{CO_2H}$, melting at 142°, is produced when hydro-camphoryl-malonic acid is heated (A. **257,** 303).

d-Hydro-camphoryl-malonic acid $C_8H_{14}\langle^{CH_2.CH(CO_2H)_2}_{CO_2H}$, melting at 178°, is obtained by the reduction of camphoryl-malonic ester (A. **257,** 301).

Camphoronic acid, *aaβ - trimethyl - tricarballylic acid* $(CH_3)_2C(COOH)—C(CH_3)(COOH)—CH_2(COOH)$ is produced in the oxidation of camphoric acid, lauronolic acid, and campholic acid with nitric acid.

It has been synthesised in the following manner. Aceto-acetic ester and α-bromiso-butyric ester, or α-dimethyl-aceto-acetic ester and brom-acetic ester, are condensed by zinc to **β-oxy-α, β-trimethyl-glutaric ester** $COOR.CH_2C(OH)(CH_3)C.(CH_3)_2COOR$, which PCl_5 converts into the ester of the β-chloro-acid, and the latter is then changed by potassium cyanide to the ester of β-cyano-*aaβ*-trimethyl-glutaric acid, the mononitrile of camphoronic acid, which is then saponified to camphoronic acid. The synthetic acid is racemic, while the camphoronic acids have the rotation of the original camphoric acids (C. 1898, I. 248 ; A. **302,** 53).

The importance of camphoronic acid in the determination of the constitution of camphor has been explained. Camphoronic acid melts at 135°, changing at the same time into *camphoro-anhydridic acid*, melting at 135° and boiling at 205° (12 mm.). The *chloride* of the latter is converted by bromine into two isomeric *bromo-camphoro-anhydridic acid chlorides* ; one of these, when boiled with water, forms the lactone of unstable oxy-camphoronic acid, *camphoranic acid*, while the other, under similar treatment, yields a stable *oxy-camphoronic acid*, melting at 248°. Camphoronic acid, upon distillation, breaks down into trimethyl-succinic anhydride, iso-butyric acid, CO_2, H_2O, and carbon.

Camphoranic acid $C_9H_{12}O_4+H_2O$, melting at 209°, is a lactonic acid which resists decomposition by alkalies very strongly. When fused with caustic potash it is readily split into trimethyl-succinic acid and oxalic acid (privately communicated by J. Bredt) :

$$(CH_3)_2C\langle^{CO}_{C(CH_3)(COOH)}\rangle CHCOOH \longrightarrow (CH_3)_2C(COOH)—CH(CH_3)COOH$$

Camphoranic acid — Trimethyl-succinic acid.

Fenchone $CH_2(CH_2).CH(C(CH_3)_2).CO$ (*Ch. Ztg.*, **29,** 1313), m.p. 6°, b.p. 193°, D_{19}, with specific gravity 0·9465 (19 mm.), $n_D=1·46306$, occurs naturally in two isomeric modifications. Of all the known ketone derivatives of terpenes this ketone is most like camphor in its behaviour.

d-Fenchone was discovered in 1890 by Wallach and Hartmann in fennel oil, while **l-fenchone** was found in 1892 by Wallach, together with pinene and thujone or tanacetone, in the oil of thuja. Potassium permanganate oxidises it to dimethyl-malonic acid, acetic acid, and oxalic acid, while prolonged heating with concentrated acid oxidises it to dimethyl-tricarballylic acid, dimethyl-malonic acid, and iso-camphoronic acid (C. 1899, I. 285). On reduction, it reverses its optical rotation and passes into d- and l-fenchyl alcohol respectively, and fenchone pinacone, m.p. 97°. On heating with P_2O_5 fenchone yields *m-cymol*, probably with previous transposition; under the action of strong sulphuric acid it is transformed into *acetyl-xylol* $CH_3CO.C_6H_3[3, 4](CH_3)_2$ (C. 1899, II. 1120). Fenchone does not combine with sodium bisulphite or phenyl-hydrazin, and forms no oxy-methylene compound. With sodium and CO_2 we obtain α- and **β-fencho-carboxylic acid** $C_{10}H_{17}O(COOH)$, m.p. 142° and 77° respectively. These seem to be α-oxy-acids (A. **300**, 294). With bromine, fenchone, at 100°, gives monobromo-fenchone $C_{10}H_{15}OBr$, b.p.$_{18}$ 131°–134°; while with phosphorus chloro-bromide, it yields tribromo-fenchane $C_{10}H_{15}Br_3$ (B. **33**, 2287). **Fenchone oxime** $C_{10}H_{16}$: NOH, m.p. 165° (active), 159° (inactive), b.p. 240°. **Fenchone semi-carbazone,** m.p. 183° (active), 172° (inactive). By heating with caustic potash to 230°, or by the action of sodium amide, fenchone, like camphor and camphenilone, is split up into **fencholic acid,** *1-methyl-3-iso-propyl-cyclo-pentane-1-carboxylic acid* $CH_2—CH—CH(CH_3)_2$ / CH_2 / $CH_2—C(CH_3)CO_2H$, m.p. 19°, b.p.$_{17}$ 152°, which has also been obtained synthetically (C. 1909, II. 212). Chloride, b.p.$_{15}$ 100°; amide, m.p. 94° (A. **369**, 71). **α-Fencholenic acid** $C_9H_{15}COOH$, liquid, b.p. 255°, and **β-fencholenic acid** $C_9H_{15}.COOH$, m.p. 73°, b.p. 260°, are formed by saponifying their nitriles, α-nitrile, b.p. 212°, β-nitrile, b.p. 218°, which are obtained together on boiling fenchone oxime with dilute sulphuric acid (C. 1899, II. 115). They have not hitherto been changed one into the other, and are therefore not mutually related like α- and β-campholenic acid. Both acids become lactones on treating with concentrated sulphuric acid: **oxy-dihydro-α-fencholenic lactone** $C_{10}H_{18}O_2$, m.p. 78°, and **oxy-dihydro-β-fencholenic lactone,** m.p. 69° (B. **39**, 2853), the latter being found also in the oxidation products of fenchyl alcohol. A third isomeric acid $C_9H_{15}COOH$, **γ-fencholenic acid,** b.p.$_{10}$ 146°, easily passing into the α-form, is produced on heating bromo-fenchone with alcoholic potash (B. **40**, 432).

Iso-fenchone $C_{10}H_{16}O$, b.p. 201°, is formed by oxidation of iso-fenchyl alcohol with chromic acid. **Oxime,** m.p. 82° (active), 133° (inactive), easily substituted with bromine, forming monobrom-iso-fenchone, m.p. 57°. By heating with caustic potash it is split up into **iso-fencholic acid** $C_{10}H_{18}O_2$, m.p. 34°; **amide,** m.p. 66°. On oxidation with $KMnO_4$, a dicarboxylic acid is formed, **iso-fencho-camphoric acid** $C_{10}H_{16}O_4$, m.p. 159° (active), 175° (inactive) (A. **362**, 194; **369**, 97).

D. Sesqui-terpene and Poly-terpene Group.

The sesqui-terpenes have the composition $C_{15}H_{24}$. They are related to the terpenes proper in a manner similar to the hemi-terpene

isoprene. The sesqui-terpenes are widespread among the ethereal oils. Some 70 have been traced hitherto, but many of these may be identical. They are slightly coloured, rather viscous oils, boiling between 250° and 280°, of a feeble and rather unpleasant odour, and many of them resinify easily, like the terpenes. On the basis of their molecular refraction, and other physical and chemical properties, we may distinguish trebly unsaturated monocyclic, doubly unsaturated bicyclic, and singly unsaturated tricyclic sesqui-terpenes. A probably aliphatic sesqui-terpene has been found in Ceylon citronella oil (C. 1899, II. 880), but completely saturated tetracyclic sesqui-terpenes are unknown. As from the terpenes proper, so from the sesqui-terpenes, oxygenated compounds of the composition $C_{15}H_{24}O$ and $C_{15}H_{26}O$ are derivable, called sesqui-terpene alcohols, and sesqui-terpene camphors, which are distinguished from the terpenes themselves by generally possessing a great power of crystallisation. Practically nothing is known of the constitution of the sesqui-terpenes. Many of them contain, perhaps, hydrated naphthalin rings (B. **36**, 1038). With halogen hydrides NOCl, N_2O_3, and N_2O_4 they sometimes form easily crystallising derivatives, which may serve for their separation and characterisation. In the following we enumerate some of the most important representatives of this group.

Cadinene, b.p. 270°, D_{16} 0·921 $[\alpha]_D = -98·56°$, is found in many ethereal oils, such as *Oleum cadinum*, cubebene oil, sandal-wood oil, angostura bark oil (C. 1898, II. 666; 1900, I. 858).

With HCl it yields a dichlorohydrate, m.p. 118°, from which, by heating with aniline or sodium acetate, cadinene can be regenerated (A. **238**, 84; C. 1908, II. 1354).

Caryo-phyllene, b.p.$_{20}$ 137°, D_{20} 0·903, found in carnation and copaiva oil. It probably consists of two isomeric hydrocarbons, the optically inactive caro-phyllene found in hop oil (*J. pr. Ch.* 2, **88**, 483), nitroso-chloride, m.p. 177°, and the active β-caryo-phyllene, nitroso-chloride, m.p. 159°; nitrosite, blue needles, m.p. 115°; dichlorohydrate, m.p. 70° (C. 1899, II. 1119). By hydration with glacial acetic acid and sulphuric acid we obtain **caryo-phyllene hydrate** $C_{15}H_{26}O$, m.p. 95°, from which, by elimination of water, a probably tricyclic hydrocarbon isomeric with caryo-phyllene, *clovene*, is obtained (A. **271**, 294; **369**, 41; B. **42**, 1062).

α-Santalene, b.p.$_9$ 118°–120°, D_{20} 0·8984, $n_D = 1·491$, and **β-santalene,** b.p.$_9$ 125°–127°, D_{20} 0·892, $n_D = 1.4932$, are contained in the first distillate of sandal-wood oil; the former is probably a tricyclic, and the latter a bicyclic, sesqui-terpene. On oxidation with ozone the α-santalene yields tricyclo-ek-santalic acid $C_{11}H_{16}O_2$, m.p. 68°, and the β-santalene bicyclo-ek-santalic acid $C_{11}H_{16}OH_2$, m.p. 64°, also obtained by disintegrating santalol (B. **40**, 3321).

Zingiberene, b.p.$_{22}$ 160°, D_{20} 0·8731, $n_D = 1·49399$, $[\alpha]_D = -73·38°$, is contained in ginger oil. Nitroso-chloride, m.p. 97°; dichlorohydrate, m.p. 169° (C. 1901, II. 1226).

Galipene is the name of a dextro-rotatory sesqui-terpene obtained from the oil of angostura bark, *Galipea officinalis* (C. 1898, II. 666).

Santalol $C_{15}H_{24}O$, b.p.$_{10}$ 161°–168°, D_{20} 0·973, forms the chief constituent of the Indian sandal-wood oil from *Santalum album*. It probably consists of a mixture of two unsaturated primary alcohols, the

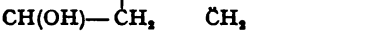
tricyclic α-santalol and the bicyclic β-santalol. α-Santalol yields on oxidation with $KMnO_4$ or ozone tri-cyclo-ek-santalic acid. Acids convert α-santalol and its derivatives into isomeric, and, probably, bicyclic compounds (B. **40,** 1120).

Patchouli alcohol $C_{15}H_{26}O$, m.p. 56°, separates out from patchouli oil in crystals (A. **279,** 394 ; C. 1904, I. 1265).

Cedrol $C_{15}H_{26}O$, m.p. 87°, $[\alpha]_D = +9° 31'$, from cedar-wood oil of *Juniperus virginiana.*

The **diterpenes** $C_{20}H_{32}$ and **polyterpenes** $(C_5H_8)_x$ are yellow, viscid oils, boiling above 300°, volatilising with steam with some difficulty, and therefore but rarely encountered in ethereal oils. They are found in many balsams and resins. Their characterisation is rendered difficult by the fact that they only yield crystalline addition products with difficulty.

Addendum.—Closely related to the polyterpenes is the **cholesterin** already discussed in Vol. I., which, from its transformations, must be regarded as a polycyclic secondary ring alcohol, with a vinyl and an iso-amyl side chain. The constitution is complex, but is probably as follows (B. **42,** 3770) :



Resins.

The resins are closely related to the terpenes, and occur with them in plants, and are also produced by their oxidation in the air. Their natural, thick solutions in the essential oils and turpentines are called *balsams* ; whereas the true *gum resins* are amorphous, mostly vitreous bodies. Their solutions in alcohol, ether, or turpentine oils constitute the commercial *varnishes.*

Most natural resins appear to consist of a mixture of different, peculiar acids, the resin acids. The alkalies dissolve them, forming *resin soaps,* from which acids again precipitate the *resin acids.* By their fusion with alkalies we obtain different benzene derivatives (resorcinol, phloro-glucin, proto-catechuic acid) ; and when they are distilled with zinc dust they yield benzenes, naphthalenes, etc.

Colophony is found in turpentine and, in the distillation of the latter, remains as a fused mass. It consists principally of **abietic acid** $C_{19}H_{28}O_2$ (sylvic acid), which can be extracted by hot alcohol, crystallises in leaflets, and melts at 139° (147°). When oxidised it yields trimellitic, iso-phthalic, and terebic acids.

On heating with sulphur it turns into retene. It is therefore probably a decahydro-retene-carboxylic acid (C. 1904, II. 1308), and thus is closely connected with *fichtelite,* a fossil resin, which has been recognised as perhydro-retene.

Gallipot resin, from *Pinus maritima,* contains **pimaric acid** $C_{20}H_{30}O_2$, which is very similar to sylvic acid and passes into the latter when distilled *in vacuo.* It melts at 210°. The latest investigations show that pimaric acid consists of three isomerides (B. **19,** 2167).

Gum lac, obtained from East India fig-trees, constitutes what is

known as shellac when fused. This is employed in the preparation of sealing-wax and varnishes.

Amber is a fossil resin, found in peat-bogs. It consists of succinic acid, two resin acids, and a volatile oil. After fusion it dissolves easily in alcohol and turpentine oil, and serves for the preparation of varnishes.

To the *gum resins*, occurring mixed with vegetables gums, and gum in the juice of plants, belong gamboge, euphorbium, asafœtida, india-rubber, and gutta-percha.

Caoutchouc, india-rubber, because of its wide applicability, is especially important. It has been obtained from tropical Euphorbiaceæ, Apocinaceæ, etc. In Brazil it is made from *Siphonia elastica*, in India from *Ficus elastica*, as well as other varieties of Ficus. Purified caoutchouc has the formula $(C_5H_8)_x$. When distilled it yields isoprene C_5H_8 (*q.v.*), which polymerises spontaneously to caoutchouc and also to dipentene.

Caoutchouc is therefore probably a polymeric **1, 5-dimethyl-cyclo-octadiene-1, 5** $\left[\begin{matrix}CH_3C—CH_2.CH_2.CH \\ \| \qquad\qquad\quad \| \\ CH.CH_2.CH_2.CCH_3\end{matrix}\right]_x$. In accordance with its unsaturated nature, it easily absorbs oxygen, halogens, and nitrous-acid gas. On prolonged treatment of a benzene solution of rubber with N_2O_3, we obtain yellow crystalline nitrosite $(C_{10}H_{15}N_3O_7)_2$, decomposing at 158°–162°, the formation of which can be used for the quantitative determination of rubber in mixtures. On distillation, india-rubber yields, among hydrocarbons of greater molecular weight, isoprene C_5H_8, which under various conditions, *e.g.* on simple heating in closed vessels, partly polymerises again into rubber (B. **33,** 779; **36,** 1937; A. **333,** 184).

$$\begin{matrix}CH_3C—CH_2.CH_2.CH \\ \| \qquad\qquad\quad \| \\ CH.CH_2.CH_2.CCH_3\end{matrix} \rightleftharpoons \begin{matrix}CH_2.C—CH:CH_2 \\ \| \qquad\quad + \\ CH_2 \qquad CH_2:CH.C.CH_3\end{matrix} \qquad \begin{matrix}CH_3 \\ \| \\ .\end{matrix}$$

This last reaction promises to be of great technical importance for the artificial production of rubber.

India-rubber takes up sulphur when it is thoroughly kneaded with it, or when it is treated with a mixture of S_2Cl_2 and CS_2 (B. **27,** R. 204, 521, 601, 609, 701, 816; **29,** R. 136).

The product is a vulcanised rubber, which continues elastic within a considerable range of temperature.

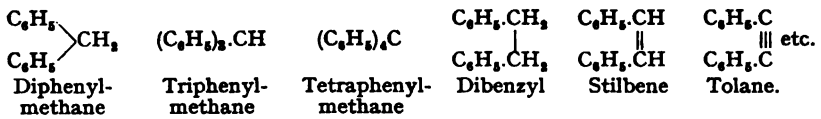
Aromatic Hydrocarbons containing several Nuclei.

A. Phenyl-benzols and Polyphenyl-fatty Hydrocarbons.

Just as alkyl groups are joined to one another, or as they are introduced into benzene and its homologues, so the benzene hydrogen atoms can be replaced by phenyl-, tolyl-, benzyl-, and other hydrocarbon residues. The products are: (1) the phenyl-benzols, in which the benzene nuclei are in immediate union:

$C_6H_5.C_6H_5$	$C_6H_5.C_6H_4CH_3$	$C_6H_4(C_6H_5)_2$	$C_6H_3(C_6H_5)_3$
Diphenyl	Phenyl-tolyl	Diphenyl-benzol	Triphenyl-benzol.

(2) The polyphenyl paraffins, olefins and acetylenes, in which the benzene residues are held together by fatty hydrocarbons :



Diphenyl-methane | Triphenyl-methane | Tetraphenyl-methane | Dibenzyl | Stilbene | Tolane.

In addition to these groups we have : B. *The aromatic hydrocarbons with condensed nuclei.*

1. Phenyl-benzol Group.

1. A. *Diphenyl Group.*—The first, or parent, hydrocarbon of this group is diphenyl or phenyl-benzol.

Diphenyl, *phenyl-benzol, biphenyl* $C_6H_5.C_6H_5$, melting at 71° and boiling at 254°, is present in slight amount in coal-tar. It is formed (1) upon conducting benzene vapours through tubes heated to redness (Berthelot, *Z. f. Ch.*, 1866, 707 ; B. **9,** 547 ; A. **230,** 5) ; (2) in the action of sodium upon the solution of bromo-benzol in ether or benzene—higher condensed hydrocarbons being produced at the same time (Fittig, A. **121,** 363 ; B. **29,** 115)—or, better, from iodo-benzol and copper powder by heating to 230° (A. **332,** 40) ; (3) from diazo-benzol chloride (*a*) by action of benzene and aluminium chloride, (*b*) with stannous chloride, (*c*) when alcohol and copper powder act upon diazo-benzol sulphate, (*d*) from the latter salt and warm benzene (B. **23,** 1226 ; **26,** 1997).

If dissolved in glacial acetic acid, and oxidised with chromic anhydride, it yields benzoic acid. Metallic sodium reduces diphenyl, dissolved in amyl alcohol, to **tetrahydro-diphenyl** $C_{12}H_{14}$, boiling at 245°. The latter readily forms a dibromide, which alcoholic potash converts into **dihydro-diphenyl** $C_{12}H_{12}$, boiling at 248° (B. **21,** 846). A dihydro-diphenyl of m.p. 66° has been obtained from phenyl-dihydro-resorcin by converting this diketone into the corresponding dihydric alcohol, and removing two molecules of water from the latter, by means of phosphorus pentoxide (A. **289,** 168). **Hexahydro-diphenyl,** *phenyl-cyclo-hexane* $C_6H_5.C_6H_{11}$, m.p. 7°, b.p. 239°, by synthesis from benzene and chloro-cyclo-hexane or cyclo-hexyl chloride with $AlCl_3$ (C. 1907, I. 1745). **Perhydro-diphenyl, dicyclo-hexyl** $C_6H_{11}.C_6H_{11}$, b.p. 235°, by reduction of diphenyl with hydrogen and nickel under pressure (C. 1907, II. 2036), or of cyclo-hexyl-cyclo-hexanol (see below) with HI, and, synthetically, from iodo-cyclo-hexane and sodium (B. **40,** 70).

Fluorene (B. **19,** R. 672) is formed when methylene chloride and aluminium chloride act upon diphenyl.

Alkylated diphenyls have been obtained : (1) By the action of nitrous acid upon the alcoholic solution of their amido-compounds (B. **17,** 468 ; **21,** 1096). (2) From the action of sodium upon the brominated alkyl-benzols (B. **4,** 396) ; this reaction gives by-products in the shape of substances of the diphenyl-methane and dibenzyl series (B. **4,** 396 ; **32,** 1056 ; **33,** 334). (3) From iodo-alkyl-benzolene by heating with powdered copper (A. **332,** 38 ; C. 1910, I. 1974). (4) From diphenyl, chloro-alkyl or ethylene, and aluminium chloride (B. **20,** R. 218). (5) From aromatic diazo-chlorides containing one

nucleus. The position of the alkyl groups is determined by oxidation, if it has not been made evident by the components :

m-Phenyl-tolyl, *m-methyl-diphenyl*	. .	b.p. 272°–277°
p-Phenyl-tolyl	m.p. +3°	,, 263°–267° (B. **26,** 1996)
m-Ethyl-diphenyl	. .	,, 283°
o_2-Ditolyl	m.p. 17·8°	,, 258°
m_2-Ditolyl, *m, m-dimethyl-diphenyl* .	. .	,, 286° (B. **25,** 1032)
o, m-Ditolyl	. .	,, 286°
p_2-Ditolyl	m.p. 122°	,, 295° (A. **332,** 44).

Hydrated derivatives of the diphenyl series are obtained synthetically by the method used in the case of the cyclo-hexenones (*q.v.*), *e.g.* **phenyl-methyl-cyclo-hexenone** $C_6H_5.CH\langle\begin{matrix}CH_2—CO\\CH_2—C(CH_3)\end{matrix}\rangle CH$, m.p. 36°, is formed from benzylidene-bis-aceto-acetic ester, and yields, on reduction, **phenyl-methyl-cyclo-hexanol** $C_6H_5.C_6H_9(CH_3)(OH)$, b.p.$_{20}$ 177°, which, on splitting off water, forms **phenyl-methyl-cyclo-hexene** $C_6H_5.C_6H_8(CH_3)$, b.p.$_{17}$ 129° (A. **303,** 259). See also Phenyl-dihydro-resorcin.

Cyclo-hexyl-2-cyclo-hexanol $C_6H_{11}.C_6H_{10}OH$, m.p. 31°, b.p. 270°, by reduction of cyclo-hexalidene-cyclo-hexanone (B. **40,** 70).

Diphenyl Substitution Products.—Each mono-substitution product of diphenyl can exist theoretically in three isomeric forms. Chlorine, bromine, the NO_2 group, and the sulpho-group prefer the p-position with reference to the point of union of the two benzene residues. o- and o, p-Derivatives are formed together with the p- and p_2-derivatives. The p_2-derivatives, having two different substituents—*e.g.* p-bromo-p-nitro-diphenyl—yield both p-bromo- and p-nitro-benzoic acids when they are oxidised (see Benzidin). The amido-diphenylenes, particularly benzidin, or p_2-diamido-diphenyl and the diphenyl-sulphonic acids, afford, as in the case of the corresponding benzene derivatives, numerous derivatives of diphenyl.

It is interesting to note that o_2-di-substitution products are known in which a bivalent atom, O and S, or a bivalent group, NH, CH_2, CO, replaces two hydrogen atoms in the ortho-position with reference to the point of union of the two benzene nuclei.

The principal representatives of such diphenylene compounds are :

Diphenylene oxide | Diphenylene sulphide | Carbazol | Fluorene | Fluorenone.

The first three will be treated in connection with the heterocyclic derivatives after furfurane, thiophene, and pyrrol, from which they can also be derived. They are formed by pyro-reactions from phenyl ether, phenyl sulphide, and diphenyl-amine.

Halogen Diphenyls.—**o-** and **p-Chloro-diphenyl** melt at 34° and boil at 267°, and at 75° and 282°, respectively. **o-** and **p-Bromo-diphenyls,** liquid, b.p. 310°. **p-Iodo-diphenyl,** m.p. 111°. **p_2-Difluoro-, p_2-dichloro-, p_2-dibromo-,** and **p_2-di-iodo-diphenyl,** m.p. 87°, 148°, 164°, and 202° respectively (A. **207,** 333 ; B. **30,** 2800).

o_2-Di-iodo-diphenyl, m.p. 108°, with chlorine yields **diphenyl-**

di-iodide tetrachloride $Cl_2IC_6H_4.C_6H_4ICl_2$, m.p. 130°–135°, from which o_2-di-iodoso- and o_2-di-iodo-phenyl are obtained. The latter, by the action of potassium iodide, passes into **diphenylene-iodonium iodide** $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>\!I.I$, m.p. 211°, also formed, besides o_2-di-iodo-diphenyl, from the tetrazo-compound of o_2-diamido-diphenyl, and is transposed on heating into the isomeric o_2-di-iodo-diphenyl (C. 1909, I. 374). On derivatives of p_2-di-iodo-diphenyl with multivalent iodine, see B. **42,** 3826.

Perchloro-diphenyl $C_{12}Cl_{10}$ does not melt at 270°. It is often produced in exhaustive chlorinations (B. **16,** 2881).

Nitro-diphenyls.—The nitration of diphenyl gives rise to o- and p-nitro- as well as to p_2- and o, p-dinitro-diphenyls.

Symmetrical di- and poly-nitro-diphenyls can be easily prepared from o- and p-halogen-nitro-benzols and from m-iodo-nitro-benzols by heating with copper powder (B. **34,** 2174). They are also obtained by the decomposition of diazonium salts of nitranilines by means of cuprous chloride or ammoniacal oxide solutions (B. **34,** 3802 ; **38,** 725 ; A. **320,** 123).

o_2- and m_2-Dinitro-diphenyls are obtained from benzidin (B. **20,** 1028).

o-, m-, and **p-Nitro-diphenyl,** m.p. 37°, 58°, and 113°.

o_2-, m_2-, p_2-, and **o, p-Dinitro-diphenyls** melt at 124°, 197°, 233°, and 93°. p_2- and o, p-Dinitro-diphenyl have also been obtained from sodium iso-diazo-nitro-benzene and nitro-benzene (B. **29,** 165).

o_2, p_2-, and **m_2, p_2-Tetranitro-diphenyl,** m.p. 163° and 186° respectively, from 1, 2, 4-chloro-dinitro- and 1, 3, 4-iodo-dinitro-benzol respectively with Cu dust.

o_2, o_2, p_2-Hexanitro-diphenyl, m.p. 238°, from picryl chloride with Cu dust.

p-Bromo-p-nitro-diphenyl, m.p. 173° (A. **174,** 218).

p_2-Dichloro-o_2-dinitro-diphenyl, m.p. 136°, from 2, 5-dichloro-nitro-benzol or 4, 2-chloro-nitraniline.

The o_2-dinitro-diphenyls are reduced by Na amalgam in alcohol, by sodium sulphide and stannous chloride in HCl, or by electrolysis, in such a manner that cyclic azoxy-compounds, phenazone oxides, and further cyclic azo-compounds, phenazones, are formed (B. **37,** 23). These compounds are dealt with in detail in connection with ortho-diazins (see Hetero-cyclic Compounds, Vol. III.) :

$$\begin{matrix}C_6H_4{-}NO_2\\ C_6H_4{-}NO_2\end{matrix} \longrightarrow \begin{matrix}C_6H_4{-}N\\ C_6H_4{-}N\end{matrix}\!\!>\!O \longrightarrow \begin{matrix}C_6H_4{-}N\\ C_6H_4{-}N\end{matrix}$$

Amido-diphenyls and **amido-ditolyls** can be prepared by the reduction of the corresponding nitro-compounds. The formation of p_2-diamido-diphenyl by the rearrangement of its isomeride hydrazo-benzol is of great technical importance, because p_2-diamido-diphenyl or benzidin is a basic substance for the preparation of substantive cotton dyes—dyes which unite directly with the cotton fibre without the aid of mordants.

o-Amido-diphenyl, melting at 45°, is also obtained from o-phenyl-benzamide by means of bromine and caustic soda (A. **279,** 266 ; B. **25,**

1974). When conducted over heated lime it forms *carbazol*. **m-Amido-diphenyl,** m.p. 30° (B. **87,** 882). **p-Amido-diphenyl,** *xenylamine,* melts at 51° and boils at 322° (A. **260,** 233). **p_2-Nitro-amido-diphenyl,** from p_2-dinitro-diphenyl, melts at 98°.

o_2-Diamido-diphenyl, m.p. 81°, and **m_2-diamido-diphenyl** have been obtained by reducing o_2- and m_2-dinitro-diphenyl. When o_2-diamido-diphenyl is heated with concentrated sulphuric acid, it yields *carbazol.* Its tetrazo-chloride is changed by potassium sulphydrate to *carbazol,* and when its aqueous solution is heated, *diphenylene oxide* is produced (B. **26,** 1703). The reduction of the *tetrazo*-compound of o_2-diamido-diphenyl gives rise to **diphenylene-o_2-dihydrazin** $\begin{matrix} C_6H_4[2]NHNH_2 \\ | \\ C_6H_4[2']NHNH_2 \end{matrix}$, m.p. 110° (B. **29,** 2270). When heated with hydrochloric acid at 150°, it breaks down easily into ammonium chloride and an **o_2-azo-diphenylene,** the so-called *phenazone.*

Benzidin, *p_2-diamido-diphenyl,* m.p. 122° (Zinin, 1845), is obtained by the reduction of p_2-dinitro-diphenyl and p_2-nitro-amido-diphenyl. It is commercially prepared by the reduction of azo-benzol in acid solution; the hydrazo-benzol, formed at first, rearranges itself to benzidin and diphenyl, or o, p-diamido-diphenyl. This is a remarkable reaction, to which attention has already been called in connection with hydrazo-benzol (A. **207,** 330).

The great insolubility of the sulphate in water affords a means of separating benzidin from diphenylin. When treated with concentrated sulphuric acid and nitric acid, one or two NO_2 groups enter in the m-position with reference to the amido-groups of benzidin. The products are o-nitro-p_2-diamido-diphenyl and o_2-dinitro-p_2-diamido-diphenyl (B. **28,** 794). m_2-Dinitro-p_2-diacetamido-diphenyl results on nitrating diaceto-benzidin. By chlorine and bromine the four H atoms are replaced in the o-position towards the amido-groups (A. **868,** 332). By oxidation with lead peroxide in indifferent solvents, benzidin first forms the unstable pp'-dipheno-quinone di-imines, and then the pp'-diamido-azo-diphenyls (cp. the analogous transformation of o-phenylene-diamine into o_2-diamido-azo-benzol) (B. **89,** 3474).

Benzidin is, on the other hand, oxidised in acid solution by permanganate, ferric chloride, potassium ferricyanide, or chromic acid, etc., to a blue dye, probably belonging to the quino-hydrones, and built up in a manner analogous to the Wurster salts (A. **868,** 324; B. **41,** 3248).

Constitution.—The p-position of the two amido-groups of benzidin (1) is evident from the oxidation of p_2-bromo-nitro-diphenyl to p-bromo- and p-nitro-benzoic acids (5, 6), because benzidin (1) is formed from p_2-dinitro-diphenyl (2), which may be rearranged to p_2-amido-nitro-diphenyl (3) and p_2-bromo-nitro-diphenyl (4) (Gustav Schultz, A. **174,** 227):

$$\begin{matrix} (1) \\ C_6H_4[4]NH_2 \\ C_6H_4[4]NH_2 \end{matrix} \leftarrow \begin{matrix} (2) \\ C_6H_4[4]NO_2 \\ C_6H_4[4]NO_2 \end{matrix} \rightarrow \begin{matrix} (3) \\ C_6H_4[4]NO_2 \\ C_6H_4[4]NH_2 \end{matrix} \rightarrow \begin{matrix} (4) \\ C_6H_4[4]NO_2 \\ C_6H_4[4]Br \end{matrix} \rightarrow \begin{cases} \rightarrow C_6H_4[4]NO_2\ CO_2H & (5) \\ \rightarrow CO_2H\ C_6H_4[4]Br & (6) \end{cases}$$

The constitution of benzidin forms the basis for *one* of the proofs of the constitution of diphenic acid; also for that of phenanthrene isomeric with anthracene.

Benzidin sulphate consists of small scales with a silvery lustre; preparation, B. **26**, R. 321. Concentrated sulphuric acid converts it into benzidin-sulphone $\frac{C_6H_3(NH_2)}{C_6H_3(NH_2)}\!>\!SO_2$ (B. **22**, 2467). **Diaceto-benzidin,** m.p. 317°. **Thionyl-benzidin** $(C_6H_4.N:SO)_2$ (B. **24**, 753). **Di-(o-nitro-benzyl-)benzidin,** m.p. 227° with decomposition (B. **29**, 1450).

o_2-o'_2-Tetrachloro- and **tetrabromo-benzidin,** m.p. 227° and 288°.

o-Nitro-p_2-diamido-diphenyl, *m-nitro-benzidin*, melts at 143° (B. **28**, 796); see Benzidin.

NN-Dimethyl-benzidin $CH_3NHC_6H_4.C_6H_4NHCH_3$, m.p. 75°, see B. **37**, 3771. On its behaviour towards oxidising agents, see B. **41**, 3250.

Tetramethyl-benzidin $(CH_3)_2NC_6H_4.C_6H_4N(CH_3)_2$, m.p. 197°, from dimethyl-aniline by oxidation with concentrated sulphuric acid at 190°–200° (B. **37**, 29). **NN_1-Diphenyl-benzidin** $C_6H_5NHC_6H_4.C_6H_4NHC_6H_5$, m.p. 242°, is formed by the action of fuming sulphuric acid upon diphenyl-amine (B. **38**, 3575).

o_2-Dinitro-p_2-diamido-diphenyl, *m-dinitro-benzidin*, melts at 214° (B. **28**, 795). **o_2-Dinitro-tetramethyl-** and **tetra-ethyl-benzidin,** red needles, m.p. 229° and 132° (B. **37**, 29, 34).

3_2-Dinitro-4_2-diaceto-diamido-diphenyl melts above 300°, and is converted by caustic potash into **3_2-dinitro-4_2-diamido-diphenyl,** *o-dinitro-benzidin*, m.p. 220° (B. **5**, 237; **20**, 1024). **5_2-Dinitro-2_2-diamido-diphenyl** (B. **25**, 128).

o, p'-Diamido-diphenyl, *diphenylin*, melts at 45° and boils at 362°. Preparation, see Benzidin (A. **207**, 348; B. **22**, 3011). **o, p_2-Triamido-diphenyl,** *m-amido-benzidin* (B. **23**, 797). **o_2, p_2-Tetramido-diphenyl,** *m_2-diamido-benzidin*, melting at 165°, is obtained from o_2-dinitro-p_2-diamido-diphenyl (see Benzidin), and by loss of ammonia becomes p_2-diamido-carbazol.

Di-p-phenylene-diamine $(NH_2)_2[2,5]C_6H_3.C_6H_3[2,5](NH_2)_2$, melting at 168°, is converted by hydrochloric acid at 180° into 5_2-diamido-carbazol (B. **25**, 131).

Diamido-dixenylamine $NH(C_6H_4.C_6H_4.NH_2)_2$, m.p. 221°, is obtained by heating benzidin with benzidin chloride (*J. pr. Ch.* 2, **61**, 103).

Benzidin Homologues.—p_2-Diamido-phenyl-m-tolyl, o-methyl-benzidin $H_2N.C_6H_4.C_6H_3(CH_3).NH_2$, is formed upon reducing a mixture of nitro-benzol and o-nitro-toluol. It melts at 90° (B. **23**, 3222).

o-Tolidin, *p_2-diamido-m_2-dimethyl-diphenyl*, from o-hydrazo-toluol, melts at 128° (B. **20**, 2017; **23**, 3252; A. **352**, 111).

m-Tolidin, *p_2-diamido-o_2-dimethyl-diphenyl*, from m-hydrazo-toluol, melts at 109°. Isomeric *ditolylin* (B. **23**, 3252) is produced at the same time.

o- and m-Hydrazo-toluols suffer under the influence of acids the *benzidin rearrangement*. p-Hydrazo-toluol, under like conditions, follows the *semidin rearrangement*.

p_2-Diamido-m_2-diethyl-diphenyl, from o-nitro-ethyl-benzol (*J. pr. Ch.* 2, **66**, 153).

Diazo-amido- and Azo-compounds of Diphenyl.—The diphenyl-tetrazo-chloride, formed by diazotation of benzidin in hydrochloric solution, unites with two molecules aniline to form:

Diphenyl - bis - diazo - amido - benzol $C_6H_5NH.N:NC_6H_4.C_6H_4N:NNC_6H_5$, reddish-yellow crystals, m.p. 180°, also obtained from benzidin

and diazo-benzol chloride. On heating with aniline and its chlorohydrate it transposes into the isomeric **diphenyl-diazo-amido-benzol** $NH_2C_6H_4N : NC_6H_4.C_6H_4N : NC_6H_4NH_2$, m.p. 159° (C. 1906, I. 1254).

pp'-Diamido-azo-biphenyl $NH_2[4]C_6H_4.C_6H_4N : NC_6H_4.C_6H_4[4]NH_2$, m.p. 287°, is formed by oxidising benzidin with PbO_2, and from pp'-amido-nitro-diphenyl by reduction with zinc dust and NaOH, and oxidation of the resultant hydrazo-compound (B. **39**, 3479).

Benzidin Dyes.—*Benzidin* yields azo-dyes, transposition products of the diazo-chloride from benzidin and amido-sulphonic acids, phenol-carboxylic acids, and phenol-sulphonic acids, which unite directly with cotton fibre (Griess, B. **22**, 2469). These dyes are obtained as sodium salts, which are prepared by adding the aqueous solution of the tetrazo-chloride to the aqueous solution of two molecules of the sodium salt of the other component.

Sodium acetate, sodium carbonate, or ammonia is added to the solution of the sodium salt to neutralise the hydrochloric acid which is liberated :

$$\left|\begin{matrix}C_6H_4N_2.Cl\\ C_6H_4N_2.Cl\end{matrix}\right. + \left|\begin{matrix}C_6H_4(OH)CO_2Na\\ C_6H_4(OH)CO_2Na\end{matrix}\right. + CO_2Na_2 = \left|\begin{matrix}C_6H_4N : N.C_6H_3(OH).CO_2Na\\ C_6H_4N : N.C_6H_3(OH).CO_2Na\end{matrix}\right. + 2NaCl + CO_2 + H_2O.$$

The diphenyl-tetrazo-chloride, which can also be readily formed in the solid state, reacts more readily with one of its diazo-groups than it does with the other (cp. B. **30**, 2800 ; **31**, 482).

The sodium salts of two different components can thus be, step by step, brought into reaction with the tetrazo-chloride, and *mixed* tetrazo-dyes (B. **19**, 1697, 1755 ; **20**, R. 273 ; **21**, R. 71) result.

Representatives of the class of benzidin dyes are :

Chrysamine, flavo-phenin $\left|\begin{matrix}C_6H_4.N : N.C_6H_3(OH).CO_2Na\\ C_6H_4.N : N.C_6H_3(OH).CO_2Na\end{matrix}\right.$, which is made from diphenyl-tetrazo-chloride and sodium salicylate (equation above) (B. **22**, 2459).

Congo yellow $\left|\begin{matrix}C_6H_4.N : N.C_6H_3(NH_2).SO_3Na\\ C_6H_4.N : N.C_6H_4.OH\end{matrix}\right.$ is obtained from diphenyl-tetrazo-chloride, phenol, and sulphanilic acid.

The preceding dyes colour cotton fibre yellow.

The first red dye brought into commerce was *Congo red*, which is formed from the interaction of diphenyl-tetrazo-chloride and sodium naphthionate. It will be brought forward again under the naphthalene azo-dyes. The β-naphthyl-amine-sulphonic acids are particularly valuable in the preparation of substantive dyes.

Substantive dyes, similar to those from benzidin, have been obtained from p_2-amido-methyl-diphenyl, *o-methyl-benzidin*, *o-* and *m-tolidins*, dianisidin, *thio-benzidin*, *thio-tolidin* (B. **20**, R. 272), p_2-diamido-benzophenone, *p_2-diamido-stilbene* (B. **21**, R. 383).

It may be said that, *as a rule*, those *substituted* benzidins (nitro- and sulpho-benzidins, tolidins, etc.) having the substituent in the meta-position (relative to the amido-group) yield *inactive* or *feeble substantive* azo-dyes. Diamido-diphenylene oxide, benzidin sulphone, and diamido-carbazol constitute exceptions. They contain a third ring-shaped chain (B. **23**, 3252, 3268 ; **24**, 1958).

It is interesting to observe that benzidin hydrochloride itself unites

with cotton. It mordants the cotton. Hence it is possible to produce the benzidin upon the fibre (B. **19,** 2014).

The "*one-sided diazotising*" of benzidin is attained through the action of a p-tetrazo-diphenyl salt upon the aqueous solution of a benzidin salt (B. **27,** 2627); compare migrations of the diazo-group. When the bis-diazo-compound of benzidin is allowed to act upon aceto-acetic ester there result, with one molecule of the ester, **cyclo-formazyl-carboxylic ester** $COOC_2H_5C\begin{cases}N.NH—C_6H_4\\ N:N—C_6H_4\end{cases}$, a reddish-brown powder, fusing with difficulty (see Formazyl-carboxylic acid); and, with two molecules of the ester, **bis-acetyl-glyoxylic ester-phenyl-hydrazone** $[CH_3COC(CO_2C_2H_5):NNHC_6H_4—]_2$, yellow needles, melting at 198° (A. **295,** 332; cp. C. 1899, I. 563). Similar compounds with malonic and cyano-acetic ester, see C. 1902, I. 721, 1205.

p-Hydrazino-diphenyl $C_6H_5.C_6H_4[4]NH.NH_2$ (B. **27,** 3105). **p_2-Di-hydrazino-diphenyl** $(C_6H_4.NHNH_2)_2$, m.p. 167° with decomposition, yields, with formaldehyde, a characteristic hydrazone (B. **32,** 1961); see also Diphenylene-o_2-dihydrazin.

Biphenyl-sulphonic Acids.—On digesting biphenyl with sulphuric acid the first product is **biphenyl-p-sulphonic acid** (its *chloride* melting at 115°, and its *amide* at 229°), and, later, **biphenyl-p_2-disulphonic acid,** melting at 72°, and its *chloride* at 203° (B. **18,** 288). When potassium-biphenyl-p-sulphonate is heated it changes to biphenyl and potassium-biphenyl-p_2-disulphonate.

Biphenyl-o_2-disulphonic acid is obtained from benzidin-o_2-disulphonic acid (A. **261,** 310).

Biphenylene sultame $\begin{matrix}C_6H_4[2]NH\\ |\\ C_6H_4[2]SO_2\end{matrix}$, m.p. 196°, in colourless crystals of strongly acid character. Formed from the diazo-compound of o-amido-benzol sulphanilide on heating in acid solution (B. **43,** 2694).

Benzidin-sulphonic Acids.—**4_2-Diamido-biphenyl-2_2-disulphonic acid** is formed from m-hydrazo-benzol-sulphonic acid (A. **261,** 310; **268,** 130; *J. pr. Ch.* 2, **66,** 558), and, when fused with caustic potash, yields 4_2-diamido-diphenylene oxide.

4_2-Diamido-biphenyl-3_2-disulphonic acid is produced on heating benzidin with ordinary sulphuric acid to 210° (B. **22,** 2466; **39,** 3341).

o-Tolidin-disulphonic acid, *4_2-diamido-5_2-dimethyl-biphenyl-2_2-disulphonic acid* (A. **270,** 359).

4_2-Dihydrazino-biphenyl-2_2-disulphonic acid $\left(C_6H_3\begin{cases}N_2H_3\\ SO_3H\end{cases}\right)_2$, see A. **261,** 323.

Oxy-biphenyls are obtained from the biphenyl derivatives by methods similar to those by which the phenols themselves are prepared from the benzene derivatives, and also in the oxidation of phenols containing a single nucleus, when they are fused with caustic potash (B. **27,** 2107).

Monoxy-biphenyls.—**p-Oxy-biphenyl** $C_6H_5.C_6H_4[4]OH$, m.p. 165° and b.p. 306°, is obtained from diazo-benzol chloride and phenol (B. **23,** 3708).

Dioxy-biphenyls.—**o_2-Dioxy-biphenyl,** *o_2-biphenol,* m.p. 109°, b.p. 326°, from biphenyl-o_2-disulphonic acid (A. **261,** 332) and from

diphenylene oxide (coal-tar) by fusing with potash (B. **34,** 1662). By fusing with zinc chloride it reverts clearly into diphenylene oxide. Its dimethyl ether, m.p. 155°, b.p. 308°, is also formed from o-iodanisol with sodium or copper dust. Ethylene bromide gives an ethylene ether, m.p. 98° (B. **35,** 302).

m-Biphenol, m.p. 123°–125°, is obtained from *o-dianisidin* and m_2-diamido-triphenyl (B. **27,** 2107). **p_2-Biphenol,** m.p. 272°, is prepared from benzidin, biphenyl-p_2-disulphonic acid, and from phenol by the action of $KMnO_4$ (B. **25,** R. 335). **o, p-Biphenol,** from diphenylin, melts at 160°. **2, 5-Dioxy-diphenyl,** *phenyl-benzo-hydroquinone* $(HO)_2[2, 5].C_6H_3C_6H_5$, m.p. 97°, is formed by reduction of phenyl-benzo-quinone (see below); and **$m_2m'_2$-tetramethyl-p_2-dioxy-diphenol** $OH[4](CH_3)_2[3, 3']C_6H_2.C_6H_2[3, 3'](CH_3)_2[4]OH$, m.p. 221°, from tetramethyl-dipheno-quinone (see below).

Tetra-oxy-biphenyls.—**Bipyro-catechin** $(HO)_2C_6H_3.C_6H_3(OH)_2$, m.p. 84°, **biresorcin,** melting at 310°, and **bihydroquinone,** m.p. 237°, result when the three dioxy-benzols are fused with sodium hydroxide (B. **11,** 1336; **12,** 503; **18,** R. 23).

Hexa-oxy-biphenyls.—**Hexa-oxy-biphenyl** $(HO)_3C_6H_2.C_6H_2(OH)_3$ is formed from pyrogallol in baryta solution by oxidation in air (B. **35,** 2954). An isomeric hexa-oxy-biphenyl has been obtained from its tetramethyl ether, **hydro-cœrulignone** $C_{16}H_{18}O_6$, m.p. 190°, by heating with concentrated HCl (B. **11,** 797). **3, 4, 5, 3', 4', 5'-hexamethoxy-biphenyl,** m.p. 126°, and **2, 3, 4, 2', 3', 4'-hexamethoxy-biphenyl,** m.p. 123°, is obtained from 5- and 4-iodo-pyrogallol-trimethyl ether with copper dust (A. **340,** 230).

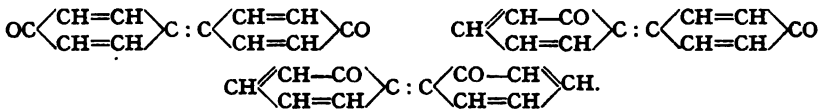
Amido-oxy-biphenyls are obtained from oxy-biphenyls (B. **22,** 335) and from the alkyl ethers of oxy-azo-derivatives, having free p-positions, by the benzidin rearrangement (B. **23,** 3256). In the coal-tar industry **o-dianisidin** or **4_2-diamido-3_2-dimethoxy-biphenyl** and **ethoxy-benzidin,** from o-nitro-anisol, are of great value. They yield violet, blue, and black substantive cotton dyes with amido-naphthalene-sulphonic acid, naphthol-sulphonic acid, and amido-naphthol-sulphonic acids: *azo-violet, benzazurin, diamine black,* etc. (B. **22,** R. 372; **24,** R. 55, 56, etc.).

2, 5-Amido-oxy-diphenyl $C_6H_5.C_6H_3[2, 5](OH)(NH_2)$, m.p. 199°, is obtained by reduction of **2, 5-nitroso-oxy-diphenyl** $C_6H_5.C_6H_3[2, 5](OH)(NO)$, generated by the action of diazo-benzol chloride upon p-nitroso-phenate of sodium. The latter, on oxidation, passes into **2, 5-nitro-oxy-diphenyl,** m.p. 126°, also obtained synthetically from benzyl-methyl-ketone $C_6H_5CH_2COCH_3$ and nitro-malonic aldehyde $NO_2CH(CHO)_2$ (C. 1905, I. 505).

Quinones of the Diphenyl Series.—**Phenyl-benzo-quinone** $C_6H_5.C_6H_3O_2$, m.p. 114°, has been obtained by the oxidation of 2, 5-amido-oxy-diphenyl, or of o-amido-diphenyl with MnO_2 and sulphuric acid. With sulphurous acid it gives a stable *quinhydrone,* also formed by oxidation in air from the 2, 5-dioxy-diphenyl produced with stronger reducing agents (A. **312,** 211; B. **37,** 878).

Special interest attaches to a number of quinone compounds of diphenyl, in which the two quinone oxygen atoms belong to different benzene rings. Regarding the quinones as carboxyl compounds, the following three fundamental forms of these so-called bi-nuclear

quinones are possible, and may be distinguished as pp'-, op'-, and oo'-dipheno-quinones:



Of these, only the pp'-dipheno-quinone could hitherto be prepared in the free state, but nitrogenated derivatives (quinone chlorimines) of the other two forms are known (A. **368**, 271).

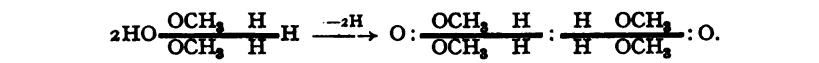
pp'-Dipheno-quinone $O : C_6H_3 : C_6H_3 : O$, decomposing at 165°, is formed by the oxidation of p-diphenol with silver oxide or lead peroxide in benzene. It crystallises in two modifications, hard spears resembling chromic acid, and fine, soft needles. In its oxidising action it resembles p-benzo-quinone, but in contrast with this it is odourless and not volatile. It can be reduced to p-diphenol, with which it unites in molecular ratio to form **dipheno-quin-hydrone**, dark-green needles decomposing at 180° (B. **38**, 1232).

m_2, m'_2-Tetramethyl-p, p'-dipheno-quinone $O : C_6H_2(CH_3)_2 : C_6H_2(CH_3)_2 : O$, m.p. about 210°, red needles, formed by the oxidation of vic-m-xylenol with chromic acid. It yields, on reduction, tetramethyl-dioxy-biphenyl, with which it forms a quin-hydrone, m.p. 201°, steel-blue flakes (B. **38**, 226).

Tetrachloro- and tetrabromo-pp'-dipheno-quinone have been obtained by the oxidation of the corresponding p-diphenol derivatives with fuming HNO_3 in glacial acetic acid. They form infusible deep-red crystals with blue surface colour, which revert to the original substances under the action of sulphurous acid (B. **18**, 224).

Cœrulignone or **cedriret** must be regarded as a tetramethoxy-pp'-dipheno-quinone.

It separates as a violet powder when crude wood-spirit is purified on a large scale by means of potassium chromate. It is further formed on oxidising dimethyl-pyrogallol from beech-wood tar with potassium chromate or ferric chloride:



Cœrulignone is insoluble in the ordinary solvents, and is precipitated in fine, steel-blue needles, from its phenol solution, by alcohol or ether. It dissolves in concentrated sulphuric acid with a beautiful blue colour. Large quantities of water colour the solution red at first. Reducing agents (tin and hydrochloric acid) convert cœrulignone into colourless hydro-cœrulignone, which changes again to the first by oxidation. Cœrulignone is, therefore, a quinone body, and may be called a *binuclear quinone*.

It unites with primary aromatic amines, forming blue dyes. It is very probable that in doing this two methoxyl groups are replaced by amino-residues (B. **30**, 235).

On the action of alcoholic HCl upon cœrulignone, see B. **31**, 615; cp. also A. **368**, 276.

A derivative of pp'-dipheno-quinone is probably also the so-called **tribromo-reso-quinone**, m.p. 214°, obtained from pentabromo-resorcin

by heating, or by treatment with silver nitrate solution, with elimination of two bromine atoms (B. **42,** 2814).

Aldehydes and Ketones of the Diphenyl Series.—**o-Phenyl-benzaldehyde** $C_6H_5.C_6H_4[2]CHO$, b.p.$_{21}$ 184°, is formed by the distillation of calcium-o-phenyl-benzoate with calcium formate. **p-Phenyl-benzaldehyde,** m.p. 57°, b.p. 184°, has been obtained from *diphenyl-glyoxylic acid* $C_6H_5C_6H_4CO.COOH$, m.p. 170°, whose ester is obtained by the condensation of diphenyl and ethoxalyl chloride by means of $AlCl_3$ (C. 1897, II. 799; 1899, I. 424). 4, 4'-Diphenyl-dialdehyde $CHO[4]C_6H_4.C_6H_4[4]CHO$, m.p. 145°; its dianile is formed by heating p-iodo-benzylidene-aniline with copper dust (A. **332,** 76).

m-Phenyl-acto-phenone $C_6H_5.C_6H_4[3]COCH_3$, m.p. 121°, from diphenyl, acetyl chloride, and $AlCl_3$ (*J. pr. Ch.* 2, **81,** 394). **Nitro-phenyl-benzaldehyde** $NO_2C_6H_4.C_6H_4CHO$ and **nitro-phenyl-aceto-phenone** $NO_2C_6H_4.C_6H_4COCH_3$ are formed from sodium iso-diazo-nitro-benzate, with benzaldehyde and aceto-phenone respectively, in the presence of acetyl chloride (B. **28,** 525). **oo'-Diacetyl-diphenyl** $CH_3CO[2]C_6H_4.C_6H_4[2]COCH_3$, m.p. 84°, see A. **363,** 305.

Biphenyl-carboxylic acids are obtained from diphenyl derivatives by reactions similar to those by which the benzene-carboxylic acids are prepared from the derivatives of benzene.

Biphenyl-monocarboxylic Acids.—There are three possible acids: **o-Phenyl-benzoic acid** $C_6H_5.C_6H_4[2]CO_2H$, melting at 111°, is produced by fusing diphenylene-ketone with caustic potash (A. **166,** 374); by the distillation of sodium salicylate with triphenyl-phosphate (*J. pr. Ch.* 2, **28,** 305); and from o-amido- and o-methyl-diphenyl. If the acid be treated with PCl_5, or if it be heated with sulphuric acid to 100°, or with lime to more elevated temperatures, diphenylene-ketone will be formed (A. **266,** 142; **279,** 259).

o-Phenyl-hexamethylene-carboxylic acid $C_6H_5[1]C_6H_{10}[2]COOH$, m.p. 150°, is synthesised from phenyl-pentamethylene dibromide with sodium-malonic ester, etc. (B. **35,** 2122).

m-Phenyl-benzoic acid, melting at 160°, results from the oxidation of m-methyl-biphenyl, of iso-diphenyl-benzol, and in the reduction of bromo-m-phenyl-benzoic acid (B. **27,** 3390).

p-Phenyl-benzoic acid, melting at 218°, is obtained from p-methyl-biphenyl, from p-diphenyl-benzol, from sodium biphenyl-sulphonate (A. **282,** 143), from p-amido-diphenyl, and by fusing benzoic acid with caustic potash. It is reduced to *p-phenyl-hexahydro-benzoic acid* $C_6H_5C_6H_{10}[4]CO_2H$, in two modifications melting at 202° and 113° respectively (A. **282,** 139). **p_2-Nitro-phenyl-benzoic acid,** melting at 222°–225°, results from the oxidation of p_2-nitro-phenyl-tolyl. It yields the corresponding *amido-acid* (B. **29,** 166) on reduction.

Biphenyl-m-acetic acid $C_6H_5.C_6H_4[3]CH_2COOH$, m.p. 153°, from m-phenyl-aceto-phenone (see above), by heating with yellow ammonium sulphide.

Oxy-biphenyl-carboxylic Acids.—The following acids are all derivatives of o-phenyl-benzoic-acid:—

6-Phenyl-salicylic acid $C_6H_5[6]C_6H_3[2](OH)CO_2H$, melting at 159°, results upon fusing 3-oxy-diphenylene-ketone and potassium hydroxide (B. **28,** 112).

2-Phenyl-m-oxy-benzoic acid $C_6H_5[2]C_6H_3[3]OH.CO_2H$, melting at

154°, is obtained as the principal product in the fusion of 6-oxy-diphenylene-ketone with potassium hydroxide (A. **284**, 307).

o-Oxy-phenyl-o-benzoic acid is only known in the form of its lactone, biphenyl-methylolid $\begin{matrix} C_6H_4[2]CO \\ | \\ C_6H_4[2]O \end{matrix}$, melting at 92·5°, which is formed as a by-product on fusing 6-oxy-diphenylene-ketone or o-oxy-fluorenone with caustic potash, in small quantities by the action of $POCl_3$ upon sodium salicylate, and when phenol acts upon the sulphate of o-diazo-benzene (A. **284**, 316). It corresponds in composition to *phenanthridone* $\begin{matrix} C_6H_4[2]CO \\ | \\ C_6H_4[2]NH \end{matrix}$, melting at 293° (see this), which is produced when bromine and caustic potash act upon diphenamic acid (A. **276**, 245).

p-Oxy-phenyl-o-benzoic acid $HO[4]C_6H_4[1]C_6H_4[2]CO_2H$, melting at 206°, is produced, together with biphenyl-methylolid and phenyl-ether-salicylic acid, by the action of phenol upon the sulphate of o-diazo-benzoic acid (A. **286**, 323).

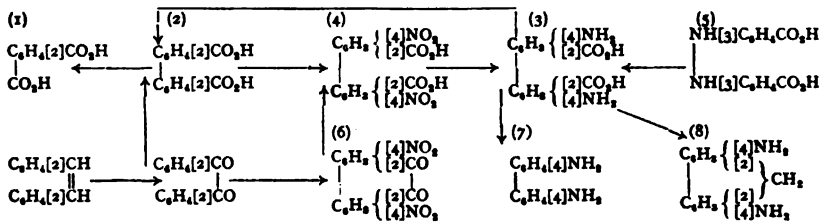
Biphenyl-dicarboxylic acids contain the two CO_2H groups, either linked to the same or to different benzene residues. *Diphenic acid* is the most important biphenyl-dicarboxylic acid.

Phenyl-iso-phthalic acid $C_6H_5C_6H_3[3, 5](COOH)_2$ melts above 310°, and is formed on boiling benzaldehyde and pyro-racemic acid with baryta water (B. **24**, 1750).

Diphenic acid, *o_2-biphenyl-dicarboxylic acid* $CO_2H[2]C_6H_4.C_6H_4[2]CO_2H$ melts at 229°.

It is formed from diazo-anthranilic acid by the action of ammoniacal cuprous oxide solution (A. **320**, 123). Its dimethyl ester, m.p. 74°, forms on heating o-iodo-benzoic ester with copper (A. **332**, 70).

It is produced in the oxidation of phenanthraquinone with a chromic acid mixture, or by boiling it with alcoholic potash. The constitution of phenanthrene follows from it. That of diphenic acid (2) is evident from its oxidation to o-phthalic acid (1) (Anschütz and Japp, B. **11**, 211) by potassium permanganate, and its formation by the deamidation of p_2-diamido-diphenyl-o_2-dicarboxylic acid (3), which is obtained on the one hand from p_2-dinitro-diphenic acid (4), and on the other by the rearrangement of m-hydrazo-benzoic acid (5) (G. Schultz, A. **204**, 95) :



In this circle of reactions there should also be included the formation of p_2-dinitro-diphenic acid by the oxidation of p_2-dinitro-phenanthraquinone (6) and the transposition of diamido-diphenic acid to benzidin (7), the constitution of which was previously deduced, and to p_2-diamido-fluorene (8).

Concentrated sulphuric acid changes diphenic acid to diphenylene-ketone-carboxylic acid. When it is digested with acetyl chloride or acetic anhydride it yields **diphenic anhydride** $\begin{matrix}C_6H_4.CO\\|\\C_6H_4.CO\end{matrix}\!\!>\!O$, melting at 213° (A. **226**, 1). This is a remarkable compound, inasmuch as it can be viewed as adipinic anhydride and contains a "seven-membered" ring. **Diphenic chloride** $\begin{matrix}C_6H_4.COCl\\|\\C_6H_4.COCl\end{matrix}$, melting at 93°, is reduced in ethereal solution by zinc and hydrochloric acid to phenanthrene-hydroquinone $\begin{matrix}C_6H_4.C(OH)\\|\;\;\|\\C_6H_4.C(OH)\end{matrix}$ (A. **247**, 268). **Diphenamino acid** $\begin{matrix}C_6H_4.CO.NH_2\\|\\C_6H_4.CO.OH\end{matrix}$, melting at 193°, is converted by a hypobromite or hypochlorite, in alkaline solution, into phenanthridone (A. **276**, 248). **Diphenimide** $\begin{matrix}C_6H_4.CO\\|\\C_6H_4.CO\end{matrix}\!\!>\!NH$, melts at 219° (A. **247**, 271).

o-, m-, and p-Nitro-diphenic acid, m.p. 248°–250° with decomposition, 268°, and 214°–216° respectively, **o_2-** and **p_2-dinitro-diphenic acid,** m.p. 303° with decomposition, and 253° respectively, are formed from the nitro- and dinitro-phenanthrene-quinones by oxidation with chromic acid mixture; in the o_2- and p_2-dinitro-acid the anhydride formation is more difficult (B. **36**, 3730, 3738). The ester of the p_2-acid is also obtained from two molecules of 2-bromo-5-nitro-benzoic ester, by heating with copper dust. In the same manner, **o_2-dinitro-biphenyl-p_2-dicarboxylic ester** is obtained from 4-bromo-3-nitro-benzoic ester (B. **34**, 2682). By reduction, the nitrated diphenic acids yield **amido-** and **diamido-diphenic acids,** from which **amido-oxy-** and **dioxy-diphenic acids** are obtained (B. **38**, 3769).

Hexa-oxy-biphenyl-o_2-dicarboxylic acid. The formula of a dilactone of this acid $\begin{matrix}OC[2]C_6H[4,\,5](OH)_2(6)O\\|\\O[6]C_6H[4,\,5](OH)_2[2]CO\end{matrix}$ probably applies to ellagic acid (*q.v.*), the oxidation product of gallic acid (B. **36**, 212).

Iso-diphenic acid (o, m′) $CO_2H[3]C_6H_4.C_6H_4[2]CO_2H$, melting at 216°, is produced when diphenylene-ketone-carboxylic acid is fused with caustic potash.

o, p′-Biphenyl-dicarboxylic acid $CO_2H[4]C_6H_4.C_6H_4[2]CO_2H$, melting at 251°, is obtained from diphenylin (B. **22**, 3019).

m_2-Biphenyl-dicarboxylic acid, m.p. 357°; its dimethyl ester, m.p. 104°, has been obtained by heating m-iodo-benzoic ester with copper dust (A. **332**, 71).

p_2-Biphenyl-dicarboxylic acid decomposes at a higher temperature. It is obtained from benzidin and by oxidising p_2-ditolyl. Its dimethyl ester, m.p. 212°, is obtained from p-iodo-benzoic ester and copper (A. **332**, 73).

p_2-Diamido-biphenyl-m_2-dicarboxylic acid is obtained from o-nitro-benzoic acid, just as p_2-diamido-diphenic acid is prepared from m-nitro-benzoic acid (B. **25**, 2797; **31**, 2574). It is converted through its tetrazo-compounds into **p_2-dioxy-biphenyl-m_2-dicarboxylic acid,** *disalicylic acid*, m.p. 302°–305°.

m_2-Dimethyl-biphenyl-p_2-dicarboxylic acid melts above 300°, is formed from o-tolidin, and is oxidised to **diphthalic acid,** *biphenyl-m_2, p_2-dicarboxylic acid* $(CO_2H)_2[3,\,4]C_6H_3.C_6H_3[3,\,4](CO_2H)_2$ (B. **26**, 2486).

I. B. **Diphenyl-benzols,** *diphenyl-phenylenes* $C_6H_4(C_6H_5)_2$.—Two such bodies are known: **m-diphenyl-benzol,** *iso-diphenyl-benzol,* melting at 85° and boiling at 369°, and **p-diphenyl-benzol,** melting at 205° and boiling at 383°. They are formed simultaneously on conducting benzene through a tube heated to redness, and by the action of diazo-benzol chloride upon diphenyl and Al_2Cl_6 (B. **26,** 1998). The p-body is also produced in the action of sodium upon a mixture of p-dibromo-benzol and bromo-benzol (A. **164,** 168). Iso-diphenyl-benzol is also prepared from m-dichloro-benzol and chloro-benzol by the action of sodium in xylol (B. **29,** R. 773).

p-Diphenyl-phenol $C_6H_3(OH)[2, 4](C_6H_5)_2$, formed by the condensation of cinnamic aldehyde and sodium phenyl-succinate, by means of acetic anhydride, the intermediately formed **diphenyl-butadiene-acetic acid** $C_6H_5CH : CH.CH : C(C_6H_5)CH_2COOH$ undergoing benzene ring condensation; the phenol, on distillation with zinc dust, gives p-diphenyl-benzol (B. **36,** 1407).

2, 6-Diphenyl-1, 4-nitro-phenol $(C_6H_5)_2[2, 6]C_6H_2[4]NO_2[1]OH$, m.p. 136°, is obtained synthetically from dibenzyl-ketone and nitro-malonic aldehyde. It has been converted into the corresponding amido-phenol, quinone, and hydroquinone (C. 1900, II. 560). The latter substance has also been obtained by way of diphenyl-nitroso-phenol, formed, besides phenyl-nitroso-phenol, from nitroso-phenol and two molecules diazo-benzol chloride (A. **312,** 227).

Di-biphenyl $C_6H_5.C_6H_4.C_6H_4.C_6H_5$, m.p. 320°, from p-iodo-biphenyl and copper (A. **332,** 52).

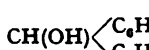
I. C. **Triphenyl-benzols** $C_6H_3(C_6H_5)_3$.—The symmetrical or [1, 3, 5] modification is formed from aceto-phenone when heated with P_2O_5, or by conducting hydrochloric acid gas into it, just as mesitylene is obtained from acetone. It melts at 169° (B. **23,** 2533). [1, 2, 3] (?)-**Triphenyl-benzol** melts at 157° (B. **26,** 69). Synthetically, several hydrated derivatives of [1, 2, 3]-triphenyl-benzol (cp. C. 1898, II. 979; 1904, I. 806; B. **32,** 2009).

I. D. **1, 2, 4, 5-Tetraphenyl-benzol** $C_6H_2(C_6H_5)_4$, m.p. 278°, from the cyclic pinacone obtained from diphenyl-dibenzoyl-butadiene (*q.v.*) (A. **302,** 210).

II. Benzyl-benzol Group.

Benzyl-benzol or diphenyl-methane is the simplest hydrocarbon of this group. The alkyl diphenyl-methanes and the compounds substituted in the benzene residues by the NO_2, NH_2, or OH groups are derived from it. If we suppose a hydrogen atom of the CH_2 group to be replaced by OH, we obtain the formula of benzo-hydrol or diphenyl-carbinol, which changes by oxidation to benzo-phenone or diphenyl-ketone. Diphenyl-methane $CH_2(C_6H_5)_2$, benzo-hydrol $HOCH(C_6H_5)_2$, and benzo-phenone $CO(C_6H_5)_2$ are the simplest representatives of the hydrocarbons, the secondary alcohols and the ketones of this group. Attached to them are the corresponding carboxylic acids—*e.g.*:

Benzo-benzoic acid



Benzo-hydrol-benzoic acid

Benzoyl-benzoic acid.

1. Hydrocarbons (Diphenyl-methanes).

Formation.—(1) From benzyl chloride, benzene and zinc dust (Zincke, A. **159,** 374), or aluminium chloride (Friedel and Crafts). (2) From formaldehyde, methylal, or methylene diacetate with benzene and sulphuric acid (Baeyer, B. **6,** 963). Both reactions are capable of wide generalisation. Thus, by use of the second reaction, substituting other aldehydes for formaldehyde, numerous hydrocarbons have been obtained in which two benzene residues are attached to the same carbon atom (see unsym. diphenyl-methane, below). (2*a*) Benzyl alcohol and benzene, by treatment with concentrated sulphuric acid, yield diphenyl-methane (B. **6,** 963). (3) By the reduction of ketones, into which the benzyl-benzols are oxidised. Diphenyl-methane derivatives are formed as by-products. (4) By the action of sodium upon mixtures of bromo-benzols and alkyl-benzols (B. **88,** 334). (5) By the oxidation of alkyl-benzols with manganese dioxide and sulphuric acid, from which we obtain tolyl-phenyl-methane (B. **88,** 464).

Diphenyl-methane $C_6H_5.CH_2.C_6H_5$, *benzyl-benzol,* is obtained (1) from benzyl chloride and benzene with zinc dust or $AlCl_3$. (2) From CH_2Cl_2 with benzene and $AlCl_3$. (3) From methylal, or (4) from benzyl alcohol, benzene, and sulphuric acid. (5) By the reduction of benzo-phenone with zinc dust or zinc and sulphuric acid, or hydriodic acid and phosphorus; and (6) upon distilling diphenyl-acetic acid with soda-lime (A. **155,** 86).

Diphenyl-methane possesses the odour of oranges. It melts at 26·5° and boils at 261°. When conducted through ignited tubes it yields diphenylene-methane or fluorene; a chromic acid mixture oxidises it to benzo-phenone, whereas concentrated nitric acid changes it to p_2-, o, p-dinitro-, and tetra-nitro-diphenyl-methane (A. **283,** 154).

Benzyl-toluenes, *phenyl-tolyl-methanes* $C_6H_5.CH_2.C_6H_4.CH_3$.—A liquid mixture of o- and p-benzyl-toluol, which cannot be separated, is obtained by the action of zinc dust on a mixture of benzyl chloride and toluol. Anthracene is formed at the same time. The pure *para*-body has been formed by heating para-phenyl-tolyl-ketone with zinc dust, and is a liquid, boiling at 285°. It appears also to be produced in the action of sodium upon p-bromo-toluol along with p-ditolyl. Bromo-mesitylene and sodium yield, together with dimesityl, a *pentamethyl-diphenyl-methane* (B. **29,** 111).

Benzyl-p-xylene boils at 294°. **Benzyl-mesitylene** melts at 36° and boils at 301°. The **benzyl-durols** melt at 60° and boil at 310°; and at 145° and 326°. **Benzyl-penta-ethyl-benzol** melts at 88° (B. **26,** R. 58). **p_2-Ditolyl-methane** melts at 22° and boils at 286°. **Dimesityl-methane** melts at 139°. The unsym. hydrocarbons were obtained according to methods 1 and 4, and the sym. according to method 1.

Nitro-diphenyl-methanes $C_6H_5.CH_2.C_6H_4.NO_2$ (A. **283,** 157).—The *ortho*-compound, prepared from o-nitro-benzyl chloride and benzene with $AlCl_3$, is liquid (B. **18,** 2402; **29,** 1303). The *meta*- and *para*-bodies are derived from meta- and para-nitro-benzyl alcohol by means of benzene and sulphuric acid. The first is an oil; the second melts at 31° (B. **16,** 2716).

o_2-Dinitro-diphenyl-methane, m.p. 159°, from p_2-diamido-o_2-dinitro-diphenyl-methane by de-amidation (*J. pr. Ch.* 2, **65**, 327).

m_2-Dinitro-diphenyl-methane, melting at 174°, is formed from m-nitro-benzyl alcohol with nitro-benzol, or from formaldehyde, nitro-benzol, and concentrated sulphuric acid (B. **27**, 2293, 2321). **m, p-Dinitro-diphenyl-methane, p-nitro-benzyl-m-nitro-benzol** melts at 103°. **p_2-Dinitro-diphenyl-methane** melts at 183°. It is obtained from diphenyl-methane along with o, p-dinitro-diphenyl-methane, melting at 118° (B. **27**, 2110; A. **194**, 363).

Tetranitro-diphenyl-methane, melting at 172°, forms dark-blue coloured salts with alcoholic potash (B. **21**, 2475).

Amido-diphenyl-methanes.—**o-Amido-diphenyl-methane** is a liquid. When its vapours are conducted over ignited lead oxide, acridin (*q.v.*) results. Nitrous acid converts it into fluorene (B. **27**, 2786). **m-** and **p-Amido-diphenyl-methane** melt at 46° and 34° respectively (B. **16**, 2718).

o_2-Diamido-diphenyl-methane, m.p. 160° (see *J. pr. Ch.* 2, **65**, 331).

p_2-Diamido-diphenyl-methanes are formed (1) from methylene dianilines on heating with aniline chlorohydrates; in this reaction amido-benzyl anilines may be formed as intermediate products, which are further transposed into diamido-diphenyl-methanes:

$$C_6H_5NH.CH_2.NHC_6H_5 \longrightarrow C_6H_5NH.CH_2C_6H_4NH_2 \longrightarrow NH_2C_6H_4CH_2C_6H_4NH_2$$

This reaction is confirmed (2) by the easy formation of diamido-diphenyl-methanes from amido-benzyl-anilines by heating with aniline chlorohydrates (C. 1900, I. 1110; cp. B. **33**, 250).

p_2-Diamido-diphenyl-methane, melting at 85°, changes completely to para-rosanilin or rosanilin when heated with aniline or o-toluidin in the presence of an oxidising agent (B. **25**, 303).

Its *tetramethyl derivative* results from dimethyl-aniline by means of $C_2H_2I_2$, CCl_3H (or CCl_4), or with methylal, or by the action of CS_2 and zinc upon dimethyl-aniline. It melts at 90°.

The hydrogen of the group CH_2 attached to *basic* radicles *is very readily replaced by sulphur*; see p_2-tetramethyl-diamido-thio-benzophenone. See A. **288**, 149, for isomeric *diamido-diphenyl-methanes.*

p_2-Diamido-o_2-dinitro-diphenyl-methane and its reduction products, see C. 1910, II. 569. p_2-Dihydrazino-diphenyl-methane $CH_2(C_6H_4.NHNH_2)_2$, m.p. 140° (*J. pr. Ch.* 2, **74**, 155).

Oxy-benzyl-benzols.—**p-Benzyl-phenol,** melting at 84° and boiling at 325° (in CO_2), is produced (1) from benzyl chloride, phenol, and zinc; (2) from benzyl alcohol, phenol with concentrated sulphuric acid, or zinc chloride; (3) from p-amido-diphenyl-methane.

The bromination products of this phenol, like the brominated phenol-alcohol bromides, can easily be converted into *methylene-quinones, e.g.* $C_6H_5CH : C_6H_2Br_2 : O + H_2O$, a yellow precipitate, easily passing into dibromo-oxy-benzo-hydrol (A. **334**, 367):

Amido-benzyl-phenols are easily obtained by the condensation of amido-benzyl alcohols with phenols (C. 1903, I. 288).

p-Dialkyl-amido-benzyl-phenols, *e.g.* $C_6H_2OHBr_2.CH_2.C_6H_4[4]N(CH_3)_2$, are formed by the action of o- and p-pseudo-phenol bromides upon tertiary anilines (A. **334**, 264).

o_2-Dioxy-diphenyl-methane is only known in the form of its anhydride, xanthene (*q.v.*).

p_2-Dioxy-diphenyl-methane is produced on fusing diphenyl-methane-disulphonic acid with KOH (A. **194**, 318). It melts at 158°. Its *dimethyl ether* is formed from anisol and methylal by the action of concentrated sulphuric acid (B. **7**, 1200), and melts at 52° (B. **7**, 1200). By exhaustive bromination it is converted into a hepta-bromide, which easily splits off HBr and turns into a *methylene-quinone* $O : C_6Br_3H : CHC_6BrH_3(OH)$, red needles, m.p. 245° (*J. pr Ch.* 2, **58**, 441 ; A. **330**, 61). Substituted p_2-dioxy-diphenyl-methanes have been obtained, in various ways, from p-oxy-benzyl alcohols, and the derived pseudo-phenol haloids (A. **356**, 124).

Multivalent phenols are easily concentrated by formaldehyde into polyoxy-diphenyl-methanes: **methylene-dipyro-catechin,** m.p. 220° with decomposition (B. **26**, 254). **Methylene-diresorcin, methylene-diorcin, methylene-dipbloro-glucin** (A. **329**, 269 ; C. 1907, I. 547).

Methylene-bis-hydro-resorcin $CH_2(C_6H_7O_2)_2$, m.p. 132°, from hydro-resorcin and formaldehyde, on boiling with acetic anhydride, yields *octohydro-xanthene-dione* $CH_2(C_6H_6O)_2O$, and with ammonia *deka-hydro-acridin-dione* $CH_2(C_6H_6O)_2NH$ (A. **309**, 356).

2. Alcohols (Benzo-hydrols).

Diphenyl-carbinol, benzo-hydrol $(C_6H_5)_2CH.OH$ melts at 68° and boils at 298° with partial decomposition into water and **benzo-hydrol ether** $[(C_6H_5)_2.CH]_2O$, melting at 109° (B. **34**, 1965). It is produced on heating diphenyl-bromo-methane with water to 150°, or, more readily, from benzo-phenone with sodium amalgam, or by heating with alcoholic potassium hydroxide and zinc dust (together with benzo-pinacone) (A. **184**, 174). Synthetically, it is prepared from formic ester with phenyl-magnesium bromide (C. 1902, II. 1209). By oxidation it passes into benzo-phenone, also by heating in the presence of palladium black (R. **36**, 2816). With quinones and quinoid substances benzo-hydrol condenses with entrance of one or two $CH(C_6H_5)_2$ groups into the quinoid nucleus (B. **32**, 2146 ; **33**, 799).

Phenyl-p-tolyl-carbinol melts at 52° (A. **194**, 265).

Diphenyl-carbinol chloride, *diphenyl-chloro-methane,* melting at 14°, is obtained from benzo-hydrol and HCl. When heated it breaks down into HCl and tetraphenyl-ethylene (B. **7**, 1128). **Diphenyl-bromo-methane,** from diphenyl-methane and bromine, melts at 45°.

Benzo-hydrylamine $NH_2.CH(C_6H_5)_2$, b.p. 288°, is obtained from diphenyl-bromo-methane and from benzo-phenon-oxime (B. **19**, 3233). The latter method has afforded the *homologous alkyl-benzo-hydroxyl-amines* (B. **24**, 2797). The *formyl derivative,* from benzo-phenone and ammonium formate at 200°–250° (B. **19**, 2129), melts at 132°. **Formamidine-benzo-hydryl** $CH(NH)NHCH(C_6H_5)_2$ is formed from prussic sesqui-chlorohydrate $2CNH.3HCl$, benzene, and $AlCl_3$ (B. **31**, 1771).

Dibenzo-hydrylamine melts at 136°.

Phenyl-benzo-hydrylamine $C_6H_5NH.CH(C_6H_5)_2$, b.p.$_{20}$ 233°, is formed when C_6H_5MgBr is attached to benzylidene-aniline and the product is decomposed with acids (B. **38**, 1767).

β-Benzo-hydryl-hydroxylamine [*diphenyl-aminol-methane*] HO.NH.

$CH(C_6H_5)_2$, m.p. 78°, is formed on boiling a solution of diphenyl-bromo-methane and acetoxime with glacial acetic acid and wate· (A. **278,** 364).

Benzo-hydryl-hydrazin $(C_6H_5)_2CH.NHNH_2$, m.p. 59°, b.p.$_{12}$ 189°, and **bis-benzo-hydryl-hydrazin** $(C_6H_5)_2CH.NHNH.CH(C_6H_5)_2$, m.p. 133°, from benzo-phenone-hydrazone and bis-benzo-phenone-hydrazone by reduction with sodium amalgam and alcohol. Benzo-hydryl-hydrazin, on boiling with HCl, splits into diphenyl-chloro-methane and hydrazin (*J. pr. Ch.* 2, **67,** 112).

o-Amido-benzo-hydrol $C_6H_4\langle^{CH(OH)C_6H_5}_{NH_2}$, m.p. 120°, is formed in the reduction of o-amido-benzo-phenone. It is capable, like o-amido-benzyl alcohol, of producing heterocyclic compounds (B. **29,** 1034). The isomeric **o-oxy-benzo-hydrylamine** $C_6H_4\langle^{CH(NH_2)C_6H_5}_{OH}$, m.p. 103°, is obtained by reduction of *phenyl-indoxazene* (C. 1898, II. 284).

p-Oxy-benzo-hydrol $HO[4]C_6H_4CH(OH)C_6H_5$, m.p. 161°, from benzoyl-phenol by reduction (A. **210,** 253). **op-Dioxy-benzo-hydrol** is formed by condensation of benzaldehyde and resorcin by means of alkali (C. 1910, I. 920). **o_2p_2-Tetramethoxy-benzo-hydrol,** m.p. 179°, from vic-iodo-resorcino-dimethyl ether, Mg, and formic ester (A. **372,** 128).

In the *aldol condensation* of benzaldehyde, or p-nitro-benzaldehyde and dimethyl-aniline, with hydrochloric acid (by $ZnCl_2$ or oxalic acid the products are triphenyl-methane derivatives) there arise : **p-nitro-p-amido-benzo-hydrol** $NO_2C_6H_4CH(OH)C_6H_4NH_2$ (C. 1901, I. 866), **p-dimethyl-amido-benzo-hydrol** $C_6H_5CH(OH).C_6H_4N(CH_3)_2$, m.p. 69°, and **p-dimethyl-amido-p-nitro-benzo-hydrol,** m.p. 96° (B. **21,** 3292). By reduction the latter compound yields **p-dimethyl-amido-p-amido-diphenyl-methane,** m.p. 165°. **p_2-Tetramethyl-diamido-benzo-hydrol,** m.p. 96°, has been obtained by the reduction of p_2-tetramethyl-diamido-benzo-phenone (B. **22,** 1879). On boiling the former with dilute mineral acids until the blue colour has disappeared, it breaks down into dimethyl-aniline and dimethyl-amido-benzaldehyde (B. **27,** 3316). In the solid condition p_2-tetramethyl-diamido-benzo-hydrol is white, while its solution is blue in colour (B. **20,** 1733, footnote). In acid solution the tetramethyl-diamido-benzo-thio-hydrol has, like auramin, perhaps a quinoid structure (B. **30,** 2803 ; **33,** 283). It is a very reactive body. On standing, or on boiling with alcohols, ethers are generated. *Methyl ether* $CH_3OCH[C_6H_4N(CH_3)_2]_2$, m.p. 72° (C. 1902, I. 471) ; with SH_2 it yields in alcoholic solution **tetramethyl-diamido-benzo-thio-hydrol** $HS.CH[C_6H_4N(CH_3)_2]_2$, m.p. 82°. With aromatic amine it spontaneously transposes into **tetramethyl-diamido-benzo-hydryl-aryl-amines** $ArNHCH[C_6H_4N(CH_3)_2]_2$, the so-called *aryl-leuc-auramines.* The simplest leucauramine $NH_2CH[C_6H_4N(CH_3)_2]_2$, m.p. 135°, is formed from auramine by reduction with sodium amalgam in alcohol ; oxidation regenerates auramine. With Am sulphide the leucauramines yield **tetramethyl-diamido-benzo-hydryl sulphide** $S[CH[C_6H_4N(CH_3)_2]_2]_2$, m.p. 172° (B. **35,** 375, 913). With compounds having a reactive CH_2 group, like malonic ester, aceto-acetic ester, etc., the hydrol easily unites with expulsion of water (C. 1910, I. 181). With

quinones and quinoid substances it condenses like benzo-hydrol itself (B. **34**, 881, etc.).

3. Ketones (Benzo-phenones).

The ketones of the benzyl-benzol group bear the same relation to the benzoic acids that the acetones bear to the fatty acids :

CH_3CO_2H	$CO(CH_3)_2$	$C_6H_5.CO_2H$	$CO(C_6H_5)_2$
Acetic acid	Acetone	Benzoic acid	Benzo-phenone.

This analogy is shown in the various methods of formation.

Methods of Formation.—(1) By oxidising (*a*) the benzyl-benzols and (*b*) the benzo-hydrols with chromic acid :

$$CH_2(C_6H_5)_2 \xrightarrow{2O} CO(C_6H_5)_2 \xleftarrow{O} HOCH(C_6H_5)_2.$$

If the CH_2 group contains alkyls or carboxyl these groups will be split off by the oxidation, with the production of ketones. If the benzene residues contain alkyl groups these are converted into carboxyl groups.

(2) By the action of hot water upon the ketone chlorides (see Benzo-phenone chloride, below).

Nuclear Syntheses.—(3) By the distillation of the calcium salts of mononucleus, aromatic monocarboxylic acids, the CO_2H groups of which are in direct union with the benzene residue :

$$(C_6H_5.CO_2)_2Ca \longrightarrow (C_6H_5)_2CO + CO_2Ca.$$

(4) By the condensation of benzoic acid or its anhydride on heating with benzene and P_2O_5.

(5) By the action of benzoyl chloride on benzene, in the presence of aluminium chloride.

Phosgene reacts in the same manner, and acid chlorides are the first products. These then change into ketones (B. **10**, 1854) :

$$C_6H_6 + COCl_2 \xrightarrow[(AlCl_3)]{-HCl} C_6H_5.COCl + C_6H_6 \xrightarrow[(AlCl_3)]{-HCl} C_6H_5COC_6H_5.$$

(6) By the action of carbon tetrachloride upon aromatic hydrocarbons and their halogen substitution products, in the presence of $AlCl_3$, benzo-phenone chlorides are obtained, which, on heating with water, turn into ketones (C. 1904, I. 283 ; 1905, I. 1248).

(7) By the action of mercury diphenyl upon the acid chlorides—*e.g.* benzoyl chloride.

Behaviour.—(1) On heating with zinc dust or hydriodic acid and amorphous phosphorus, the ketones sustain a reduction of the CO group and revert to the hydrocarbons ; for example, benzo-phenone yields diphenyl-methane. (2) Sodium amalgam changes them to secondary alcohols (benzo-hydrols) and pinacones. (3) Splitting up of alkylated benzo-phenones by heating with phosphoric acid, HI or HCl, into hydrocarbons and carboxylic acids (see B. **32**, 1565, 1908).

Benzo-phenone, diphenyl-ketone $CO(C_6H_5)_2$, is known in two modifications, the unstable (labile), melting at 26°, and produced on boiling the stable form, melting at 46°. The unstable modification slowly reverts to the more stable variety. This takes place rapidly, and with

a very perceptible evolution of heat, upon touching it, with a trace of the stable variety (B. **26,** R. 380; C. 1898, I. 1177; 1900, I. 340). It boils at 307° (760 mm.) and at 162° (12 mm.). It is produced according to the general methods: (1) by oxidising diphenyl-methane, unsymmetrical diphenyl-ethane, benzo-hydrol, diphenyl-acetic acid, etc.; (2) from benzo-phenone chloride; (3) by the distillation of calcium benzoate (Péligot, A. **12,** 41); (4) by the action of P_2O_5 upon benzoic acid and benzene; (5) from phosgene or benzoyl chloride, benzene and aluminium chloride; and (6) from benzoyl chloride and mercury diphenyl. It is also found with benzoic acid and triphenyl-carbinol (7) among the products of the action of CO_2 upon C_6H_5MgBr (B. **36,** 3005). On fusing with potassium hydrate it dissolves into benzoic acid and benzene, and on heating with sodium amide, in benzene solution, into benzamide and benzene (C. 1909, II. 22). It is converted into diphenyl-methane, benzol-hydrol, and benzo-pinacone by reduction. **Hexahydro-benzo-phenone,** m.p. 54°, from hexahydro-benzoyl chloride, benzene, and $AlCl_3$ (B. **30,** 1940).

Benzo-phenone Homologues.—**o-Phenyl-tolyl-ketone,** b.p. 315°, when conducted over heated lead oxide, passes into anthra-quinone (*q.v.*), while it yields anthracene when heated with zinc dust (B. **6,** 754). **m-Phenyl-tolyl ketone** boils at 314°.

p-Tolyl-phenyl ketone is known in two modifications: the unstable (labile) form melts at 55°; it is hexagonal. The stable form, m.p. 59°, is monoclinic (A. **189,** 84; B. **12,** 2299).

p-Ditolyl ketone melts at 92° and boils at 333°. **Benzoyl-xylol** melts at 36° and boils at 317° (B. **17,** 2847). **Benzoyl-mesitylene** melts at 36° and boils at 317°. Mesitoyl-mesitylene, m.p. 85° (*J. pr. Ch.* 2, **35,** 486), etc. All these are most conveniently prepared by method 5.

Derivatives of Benzo-phenone obtained by the Replacement of Oxygen.—**Benzo-phenone chloride,** *diphenyl-dichloro-methane* $CCl_2(C_6H_5)_2$, boiling at 193° (30 mm.), is produced when PCl_5 acts upon benzo-phenone. Also by the action of benzene upon carbon tetrachloride in the presence of $AlCl_3$ (C. 1905, I. 1248).

When heated with water it reverts to benzo-phenone, while with silver it yields tetraphenyl-ethylene, and with zinc dust tetraphenyl-ethylene, α- and β-benzo-pinacolin (B. **29,** 1790). By transposition with two molecules sodium azide, nitrogen is split off, and N, **α-diphenyl-tetrazol** $C_6H_5C\begin{matrix}N(C_6H_5).N\\ \|\\ N\text{———}N\end{matrix}$ is formed (B. **42,** 3359).

Benzo-phenone bromide $CBr_2(C_6H_5)_2$ is produced on dropping bromine into diphenyl-methane heated to 150°.

Acetals of benzo-phenone are obtained from benzo-phenone chloride with sodium alcoholates, as well as from benzo-phenone and ortho-formic ethers. Benzo-phenone dimethyl and diethyl acetals melt at 107° and 52°, and boil at 289° and 295° respectively (B. **29,** 2932; R. 774).

Thio-benzo-phenone $CS(C_6H_5)_2$ is derived from benzene by means of thio-phosgene, CS_2Cl_2, and aluminium chloride. In this reaction the phenol ethers react more readily than the hydrocarbons (B. **28,** 2869). Thio-benzo-phenone is further produced by the action of phosphorus sulphide upon benzo-phenone, but best of all when an alcoholic solution

of potassium sulphide reacts with benzo-phenone chloride. It is an intensely blue-coloured oil, which congeals at lower temperatures to blue needles, and under a pressure of 14 mm. distils at 174°. The thio-benzo-phenones, when acted upon with metallic copper, yield tetraphenyl-ethylene (B. **29**, 2944).

Benzo-phenone-diethyl- and **dibenzyl-mercaptol** $(C_6H_5)_2C(SCH_2C_6H_5)_2$ m.p. 144°, on careful oxidation, yield the corresponding sulphonals, m.p. 137° and 208° (B. **35**, 2343).

Diphenyl-dinitro-methane $(C_6H_5)_2C(N_2O_4)$, melting at 78°, results upon saturating a solution of benzo-phenone-oxime in ether with nitrogen tetroxide. It is changed back to benzo-phenone-oxime with zinc dust and glacial acetic acid. Benzo-hydrylamine is also formed (B. **28**, 3490).

Imino-benzo-phenone $(C_6H_5)_2C{=}NH$ is a colourless oil, obtained in the action of dry ammonia upon a chloroform solution of *amido-benzo-phenone chlorohydrate*. The chlorohydrate results when benzo-phenone chloride is heated with urethane to 130°. **Phenyl-benzal-sultime** $C_6H_4\langle^{C(C_6H_5)}_{SO_2}\rangle N$, melting at 164°, should be viewed as a derivative of imino-benzo-phenone, produced in the condensation of pseudo-saccharin chloride with benzene and aluminium chloride (B. **29**, 2296).

Phenyl-imino-benzo-phenone, *benzo-phenone-anile* $(C_6H_5)_2C{=}N.C_6H_5$, melting at 116°, is formed from benzo-phenone chloride and aniline (A. **187**, 199), or benzo-phenone and aniline at 240°–250°, as well as by the action of C_6H_5MgBr upon phenyl-imino-benzoic ester $C_6H_5C(OCH_3) : NC_6H_5$ (C. 1906, I. 1431). It forms unstable salts with acids, and with methyl iodide an addition product, m.p. 202° (B. **35**, 2615). A series of o-substituted benzo-phenone-aniles, all coloured more or less strongly yellow (cp. auramin) have been obtained from the corresponding ketones by heating with aniline in the presence of sulphuric acid (B. **32**, 1683).

Benzo-phenonoxime $(C_6H_5)_2C : N.OH$, melting at 140°, is known in only one modification (for the possible existence of an unstable form, consult B. **28**, R. 1008), while unsymmetrical benzo-phenones—*e.g.* bromo-benzo-phenone and phenyl-tolyl-ketone—each form two oximes (B. **28**, 2776).

Hexahydro-benzo-phenone also forms two oximes—α-, m.p. 158°; β-, m.p. 111°—the first of which, on transformation, yields benzoyl-amido-hexamethylene, while the second yields hexahydro-benzanilide (B. **30**, 2862).

Benzo-phenone-hydrazone $(C_6H_5)_2C : NNH_2$, m.p. 98°, and **bis-benzo-phenone-hydrazone,** *diphenyl-ketazin* $(C_6H_5)_2C : N.N : C(C_6H_5)_2$, m.p. 162° (*J. pr. Ch.* 2, **44**, 194). **Benzo-phenone-semi-carbazone,** m.p. 165°. The *phenyl-hydrazone* $(C_6H_5)_2C : N_2H.C_6H_5$ melts at 137° (B. **19**, R. 302).

Benzo-phenone Halogen Derivatives are mostly produced by method 5 (p. 567). **o-Bromo-benzo-phenone,** melting at 42°, is noteworthy because of the mobility of its bromine atom. If **o-bromo-benzo-phenone-oxime**, melting at 132°, be acted upon with caustic alkali it splits off hydrogen bromide and becomes *phenyl-indoxazene* $C_6H_4\langle^{C(C_6H_5)}_{O}\rangle N$

(B. **27**, 1452), while m- and p-bromo-benzo-phenone, on the other hand, yield with o-bromo-benzo-phenone two isomeric oximes (B. **25**, 3292 ; A. **264**, 152, 171).

The sym. **m-, p-dibromo-benzo-phenones** $(BrC_6H_4)_2CO$, melting at 142° and 171°, yield but *one oxime* (A. **264**, 160). **o-, p-Dibromo-benzo-phenone**, melting at 52°, yields *one oxime*, melting at 141° ; this can be readily rearranged to p-bromo-phenyl-indoxazene (B. **27**, 1453).

o-Chloro-benzo-phenone-oxime shows less readily, and **o-Iodo-benzo-phenone-oxime** more readily, than *o-bromo-benzo-phenone-oxime* the formation of phenyl-indoxazene (B. **26**, 1250).

Benzo-phenone hexachloride $C_6H_5COC_6H_5Cl_6$, m.p. 215°, from benzo-phenone and chlorine in chloroform, on heating gives **trichloro-benzo-phenone** $C_6H_5COC_6H_2Cl_3$, m.p. 131° (C. 1898, I. 1178).

Nitro-benzo-phenones.—**o-, m-,** and **p-Nitro-benzo-phenone** melt at 195°, 94°, and 138° (B. **16**, 2717 ; **18**, 2401 ; *J. pr. Ch.* 2, **65**, 308). Phenyl-indoxazene is produced when the oxime of the o-body is boiled with caustic soda (B. **26**, 1250). On heating at ordinary pressures it forms acridone, probably by way of phenyl-anthranile (B. **42**, 591).

o_2-, m_2-, p_2-Dinitro-benzo-phenone melt at 188°, 148°, and 189°. **o, n-, o, p-,** and **m, p-Dinitro-benzo-phenone** $(NO_2C_6H_4)_2CO$ melt at 126°, 196°, and 172°. **o_2-** and **o, n-Dinitro-benzo-phenones** are formed in the nitration of benzo-phenone (A. **283**, 164 ; B. **27**, 2111). **o_2, p_2-Tetranitro-benzo-phenone** melts at 225° (B. **27**, 2318). Other substituted benzo-phenones are described in the A. **286**, 306, etc.

c-Phenyl-anthranile $C_6H_4\begin{cases}C(C_6H_5)\\ \dot{N}\end{cases}\!\!>O$, feebly yellow crystals of m.p. 53°, may be regarded as an inner anhydride of o-hydroxylamino-benzo-phenone. Following anthranile and c-methyl-anthranile, it is obtained by reduction of o-nitro-aceto-phenone with tin and glacial acetic acid, or by oxidation of o-amido-aceto-phenone with Caro's acid (B. **42**, 1723), and, in small quantities, by the condensation of o-nitro-benzaldehyde and benzene, by means of concentrated H_2SO_4 (B. **41**, 1845). On heating at ordinary pressure it transposes into the isomeric acridone (B. **42**, 592). The same transformation is also produced by the simultaneous action of sulphuric and nitrous acids, probably by way of nitroso-o-hydroxylamino-benzo-phenone (B. **42**, 1716). Cp. the analogous breaking up of anthranile, and the transposition of c-methyl-anthranile into indoxyl. Derivatives of phenyl-anthranile are probably represented by a series of compounds obtained by the condensation of o-nitro-benzaldehyde with tertiary anilines and phenols, by means of concentrated HCl (B. **42**, 1714).

Amido-benzo-phenones are obtained from nitro-benzo-phenones, from benzoic acid, dimethyl-aniline and P_2O_5, benzoyl chloride, phthalanile and $ZnCl_2$ (B. **14**, 1838), etc. **o-, m-, p-Amido-benzo-phenone** melt at 106°, 87°, and 124°. o-Amido-benzo-phenone is made from toluol-sulphon-anthranilic acid chloride, with benzene and $AlCl_3$, and saponification of the resulting toluol-sulphon-amido-benzo-phenone (B. **35**, 4273 ; **39**, 4332). Or from the amide of o-benzoyl-benzoic acid by means of sodium hypo-bromite (B. **27**, 3483 ; A. **291**, 8). A mixture of o- and p-amino-benzo-phenone in the form of their benzoyl derivatives $C_6H_5CONHC_6H_4COC_6H_5$ is obtained by intramolecular atomic migration from the *intermediate dibenzoyl-aniline* $(C_6H_5CO)_2NC_6H_5$ on

heating aniline with two molecules benzoyl chloride to 220° (C. 1903, I. 924; 1904, I. 1404).

o-Amido-benzo-phenone-oxime, m.p. 156°, is rearranged at high temperatures by hydrochloric acid into o-phenylene-benzamidin (B. **24,** 2385). **Acetyl-o-amido-benzo-phenone,** m.p. 89°. **p-Dimethyl-amido-benzo-phenone, p-benzoyl-dimethyl-aniline,** m.p. 90°, is also formed on heating *malachite green* with concentrated hydrochloric acid at 180° (A. **217,** 257; B. **21,** 3293; A. **307,** 307), and by heating dimethyl-aniline-phthaloylic acid. On further derivatives of p-amido-benzo-phenone, see A. **311,** 147.

Ring-formations of o-Amido-benzo-phenone.—(1) *Acridone* is produced when o-amido-benzo-phenone is heated with lead oxide (B. **27,** 3484). (2) Nitrous acid converts this o-body into *fluorenone* or *diphenylene-ketone* (B. **27,** 3484). (3) *Phenyl-indoxazene* is readily obtained from o-amido-benzo-phenone-oxime and nitrous acid (B. **26,** 1667). (4) When acetyl-o-amido-benzo-phenone is heated with alcoholic ammonia it condenses to α-phenyl-β-methyl-quinazolin (B. **25,** 3082). (5) *Acetyl-phenyl-isindazol* (B. **24,** 2383; **29,** 1255) results when acetyl-o-amido-benzo-phenone-oxime is acted upon by acetic anhydride. (6) o-Amido-benzo-phenone condenses with acetone and sodium hydroxide to α-methyl-γ-phenyl-quinolin (B. **18,** 2405). (7) When the chlorohydrate of o-amido-benzo-phenone is heated water is eliminated, and there results an *anhydro-bis-o-amido-benzo-phenone,* which probably contains an " 8-membered " ring (B. **29,** 1272):

1. $NH_2[2]C_6H_4 \diagdown \atop C_6H_5 \diagup CO \xrightarrow{PbO} NH\langle \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} \rangle CO$ — Acridone

2. $NH_2[2]C_6H_4 \diagdown \atop C_6H_5 \diagup CO \xrightarrow[-N_2-2H_2O]{NO.OH} \begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix} \rangle CO$ — Fluorenone or diphenylene-ketone

3. $C_6H_4\langle \begin{matrix} C\langle \begin{matrix} C_6H_5 \\ N.OH \end{matrix} \\ NH_2 \end{matrix} \xrightarrow[-N_2-2H_2O]{NO.OH} C_6H_4\langle \begin{matrix} C(C_6H_5) \\ O\text{——} \end{matrix} \rangle N$ — Phenyl-indoxazene

4. $C_6H_4\langle \begin{matrix} CO.C_6H_5 \\ NH.CO.CH_3 \end{matrix} \xrightarrow{NH_3} C_6H_4\langle \begin{matrix} C(C_6H_5) : N \\ N\text{═══}CCH_3 \end{matrix}$ — α-Phenyl-β-methyl-quinazolin

5. $C_6H_4\langle \begin{matrix} C\langle \begin{matrix} C_6H_5 \\ N.OH \end{matrix} \\ NH.CO.CH_3 \end{matrix} \longrightarrow C_6H_4\langle \begin{matrix} C(C_6H_5) \\ N(COCH_3) \end{matrix} \rangle N$ — Acetyl-phenyl-isindazol

6. $C_6H_4\langle \begin{matrix} CO.C_6H_5 \\ NH_2 \end{matrix} \xrightarrow{CH_3CO.CH_3} C_6H_4\langle \begin{matrix} C(C_6H_5) : CH \\ N\text{═══}C.CH_3 \end{matrix}$ — α-Methyl-γ-phenyl-quinolin

7. $2C_6H_4\langle \begin{matrix} COC_6H_5 \\ NH_2 \end{matrix} \xrightarrow{-2H_2O} C_6H_4\langle \begin{matrix} C(C_6H_5) : N \\ N : C(C_6H_5) \end{matrix} \rangle C_6H_4$ — Anhydro-bis-o-amido-benzo-phenone.

Diamido-benzo-phenones.—**o_2-, m_2-, p_2-Diamido-benzo-phenones** melt at 134°, 173°, and 239° respectively. Nitrous acid converts the o-body into xanthone (*q.v.*) and o-oxy-fluorenone (B. **28,** 111). p_2-Diamido-benzo-phenone yields substantive cotton dyes (B. **22,** 988).

Tetramethyl-p_2-diamido-benzo-phenone, Miehler's ketone $CO\langle \begin{matrix} C_6H_4.N(CH_3)_2 \\ C_6H_4.N(CH_3)_2 \end{matrix}$, results upon heating hexamethyl violet with hydrochloric acid (B. **19,** 109). It is technically prepared by the action of $COCl_2$ upon dimethyl-aniline in the presence of $AlCl_3$. It melts at 173°. Nitrous acid converts it into nitroso-trimethyl-diamido-benzo-phenone

(B. **24,** 3198). Dimethyl-aniline and PCl_3 convert it into methyl violet, while it yields *Victoria blue* with phenyl-naphthylamine. Its *oxime* melts at 233° (B. **19,** 1852). Its *hydrazone* melts at 174° (B. **35,** 366). With two molecules dimethyl sulphate the ketone combines to form a bis-quaternary ammonium salt (*J. pr. Ch.* 2, **66,** 393).

Tetramethyl-p_2-diamido-thio-benzo-phenone $CS[C_6H_4.N(CH_3)_2]_2$, results from the action of hydrogen sulphide upon an alcoholic auramin solution heated to 60°, or it can be prepared from dimethyl-aniline and $CSCl_2$. It consists of ruby-red crystalline flakes with a blue lustre or a cantharides-green crystalline powder, melting at 202° (B. **20,** 3266, 3290; C. 1898, I. 1029); on heating with alcoholic NH_3 under pressure it forms auramin base quantitatively.

Tetramethyl-p_2-diamido-benzo-phenone imide, auramin base $[(CH_3)_2NC_6H_4]_2C : NH$, m.p. 136°, combines with dimethyl sulphate to form the methyl sulphate of methyl-auramin (*J. pr. Ch.* 2, **66,** 387). The dyestuff *auramin* is the chlorohydrate of the auramin base $[(CH_3)_2NC_6H_4]_2C : NH_2Cl$, or of a quinoid pseudo-form of it $NH_2C\langle^{C_6H_4 : N(CH_3)_2Cl}_{C_6H_4N(CH_3)_2}$ (A. **381,** 234).

Auramin results when tetramethyl-diamido-benzo-phenone is heated with ammonium chloride and zinc chloride, as well as from p-dimethyl-amido-benzamide by the action of dimethyl-aniline and zinc chloride (B. **28,** R. 86). Perfectly analogous dyestuffs are obtained from the primary anilines and diamines (B. **20,** 2844; **28,** R. 65). **Auramin,** golden-yellow flakes, is important as a cotton dye. Cotton mordanted with tannin is coloured a beautiful yellow by this salt.

Potassium cyanide changes it to the nitrile of the corresponding tetramethyl-diamido-diphenyl-acetic acid (B. **27,** 3294).

o, m-, o, p-, m, p-Diamido-benzo-phenones melt at 80°, 128°, and 126° respectively (A. **283,** 149; B. **28,** 111).

Benzo-phenone-o-sulphonic acid $C_6H_5COC_6H_4[2]SO_3H$ from sulpho-benzoic anhydride with benzene and $AlCl_3$ (B. **33,** 3486).

Benzo-phenone-3, 3 (?)-disulphonic acid $(SO_3HC_6H_4)_2CO$; chloride, m.p. 138° (C. 1898, II. 347).

Oxy-benzo-phenones are formed: (1) From amido-benzo-phenones; in this change the o-amido-benzo-phenones pass chiefly into fluorenones. (2) By decomposing the xanthones, which may be viewed as cyclic phenyl ethers of o_2-dioxy-benzo-phenones, with caustic potash. (3) By the condensation of benzoic acids or oxy-benzoic acids and phenols with zinc chloride or phosphorus oxy-chloride (B. **26,** R. 587), sulphuric acid, or tin tetrachloride (B. **23,** R. 43, 188; **24,** 967). (4) From phenols by means of benzoyl chloride, zinc dust, or zinc chloride, or aluminium chloride (B. **12,** 261). (5) By the action of benzo-trichloride and zinc oxide (B. **10,** 1969) upon phenols or their benzoyl esters. (6) By the action of alkalies upon benzo-trichloride and phenols (B. **24,** 3677). (7) From the phenol-carboxylic chlorides or their methyl-acetyl- or carbo-methoxy derivatives by condensation with benzene and $AlCl_3$ (A. **346,** 381; B. **42,** 1015).

Oxy-benzo-phenones containing but one Hydroxyl Group in the Benzene Nucleus.—**o-Oxy-benzo-phenone,** *o-benzoyl-phenol,* melting at 41°, is produced, together with the phenyl ester of benzoic acid, by the 6th method of formation; also from phenyl-indoxazene upon heating it

with hydriodic acid and phosphorus (B. **29,** R. 350). The best method, however, consists in treating methyl-salicylic chloride with benzene and aluminium chloride (B. **35,** 2811). **o-Methoxy-benzo-phenone,** m.p. 39°, see B. **1,** 332. **o-Oxy-benzo-phenone anile,** m.p. 138°.

m-Oxy-benzo-benone, melting at 116°, is produced according to methods 1, 4, 5, and 7 (B. **25,** 3533). m- and p-Methoxy-benzo-phenone, m.p. 37° and 137° respectively, b.p. 343° and 355°, from m- and p-methoxy-benzoyl chloride with benzene and $AlCl_3$ (B. **35,** 2813).

o_2-, m_2-, p_2-Dioxy-benzo-phenones melt at 173°, 162°, and 210°, and **o, m-, o, p-Dioxy-benzo-phenones** melt at 126° and 142°. They are obtained from the corresponding diamido-benzo-phenones.

o_2-Dioxy-benzo-phenone is also made from its anhydride, xanthone or diphenylene ketone oxide, by careful fusion with potassium hydrate (B. **19,** 2609). o, p-, and p_2-Dioxy-benzo-phenones are also produced in the condensation of salicylic acid and phenol with tin tetrachloride (A. **354,** 177). p_2-Dioxy-benzo-phenone appears also in the decomposition of aurin, benzaurin, phenol-phthaleïn, and rosanilin upon heating them with water and caustic potash (B. **16,** 1931). *m, p-Dioxy-benzo-phenone,* m.p. 206°, from the diamido-compound.

Oxy-benzo-phenones containing more than one Hydroxyl attached to the Benzene Nucleus.—These are prepared mainly by methods 1 and 3. Mention must be made of the ketones obtained from pyrogallic acid and gallic acid, for they, like aurine, are dyes.

The dyestuff prepared from benzoic acid and pyrogallol melts at 140°. It bears the name *aurin yellow* A in trade (A. **269,** 295; B. **32,** 1686). Isomeric with the latter is the **2, 3, 4, 5-trioxy-benzo-phenone,** m.p. 176°, obtained from trimethoxy-galloyl chloride, benzene, and $AlCl_3$ (B. **42,** 1015).

2, 5-Dioxy-benzo-phenone $C_6H_5COC_6H_3[2, 5](OH)_2$, melting at 125°, is obtained from benzaldehyde and quinone, exposed to sunlight (B. **24,** 1340; **41,** 143).

o_2 p_2-Tetraoxy-benzo-phenone $[(OH)_2C_6H_3]_2CO$ is obtained on melting up fluorescein chloride with soda. On heating it passes into dioxy-xanthane (B. **32,** 2103). **2, 5, 2′, 5′-Tetramethoxy-benzo-phenone,** m.p. 109°, from iodo-hydroquinone-dimethyl ether, Mg, and CO_2 (B. **41,** 4423).

The barks of *coto* and *paracoto*, found in Bolivia, and possessing therapeutic value, contain a series of benzo-phenone derivatives. They are:

Cotoïn $C_6H_5.CO.C_6H_2(OH)_2(OCH_3)$, m.p. 130°.

Hydrocotoïn $C_6H_5.CO.C_6H_2(OH)(OCH_3)_2$, m.p. 98°.

Methyl-hydrocotoïn $C_6H_5.CO.C_6H_2(OCH_3)_3$, melting at 113° (B. **25,** 1119; **26,** 2340; **27,** 419), which are methyl ethers of benzoyl phloroglucin; and **protocotoïn** $(CH_3O)_2(HO).C_6H_2.CO.C_6H_3(O_2CH_2)$, m.p. 141°, as well as **methyl-protocotoïn** $(CH_3O)_3.C_6H_2.CO.C_6H_3(O_2CH_2)$, m.p. 134°, derivatives of 1, 3, 5-trioxy-benzo-proto-catechone. During the oxidation of protocotoïn with permanganate, we obtain aceto-piperone (B. **34,** 1468; see also C. 1907, I. 817). Most closely related with these compounds is, according to recent investigations (B. **39,** 4014), the previously mentioned **maclurin** $(OH)_2[3, 4]C_6H_3.CO.C_6H_2[2, 4, 6](OH)_3$, which, on heating with concentrated KOH, decomposes into proto-catechuic acid and phloro-glucin. The pentamethyl ether,

formed by methylation with dimethyl sulphate, and melting at 157°, has been obtained synthetically from veratroyl chlorid phloro-glucin-trimethyl ether, and $AlCl_3$ (B. **39**, 4022).

4. Carboxylic Acids of the Diphenyl-metane Group.

There are three classes of these acids: A. *Diphenyl-methane Carboxylic Acids*; B. *Benzo-hydrol Carboxylic Acids* C. *Benzo-phenone Carboxylic Acids.*

A. *Diphenyl-methane Carboxylic Acids.*—**o-, m-, p-Benzyl-benzoic acids** $C_6H_5.CH_2.C_6H_4.CO_2H$ melt at 117°, 107°, and 154°. When the o-acid is digested with sulphuric acid, *anthranol* (*q.v.*) is produced (B. **25**, 3022; **27**, 2789; A. **291**, 17; B. **9**, 633).

o-Cyano-diphenyl-methane, m.p. 19° and b.p. 313°, is obtained from o-cyano-benzyl chloride by means of benzene and aluminium chloride as well as from o-amido-diphenyl-methane.

Benzyl-iso- and **terephthalic acid** $C_6H_5.CH_2.C_6H_3(CO_2H)$, see B. **9**, 1765.

Diphenyl-methane-o_2-dicarboxylic acid $CH_2(C_6H_4[2]CO_2H)_2$, m.p. 254°, results from the reduction of the lactone of benzo-hydrol-o_2-dicarboxylic acid, and that of the dilactone of benzo-phenone-o_2-dicarboxylic acid. Concentrated sulphuric acid changes it to anthranol-carboxylic acid (A. **242**, 253).

Diphenyl-methane-m_2-dicarboxylic acid melts at 220°–225°. Diphenyl-methane-p-dicarboxylic acid melts at 290° (B. **27**, 2324). **Diphenyl-methane-o, p-dicarboxylic acid,** m.p. 220° (A. **309**, 115).

B. *Benzo-hydrol-carboxylic Acids.*—**Benzo-hydryl-benzoic acid lactone,** *phenyl phthalide* $C_6H_4\begin{cases}[1]CH \\ [2]COO\end{cases}C$, m.p. 115°, is formed by the reduction of o-benzoyl-benzoic acid, and by the breaking down of benzo-hydrol-o_2-carboxylic acid on the application of heat. The acid corresponding to the lactone is not capable of existing as such; its salts, however, are known. PCl_5 converts the lactone into anthraquinone (B. **21**, 2005).

o-Cyano-benzo-hydrol $C_6H_5(CHOH)C_6H_4[2]CN$ has been prepared from *o-cyano-diphenyl-chloro-methane* $C_6H_5CHCl.C_6H_4CN$, the reaction product from chlorine and cyano-diphenyl-methane (B. **29**, 1315). **m-** and **p-Benzo-hydryl-benzoic acid** melt at 121° and at 164° (A. **220**, 242). **p-Tolyl-phthalide** melts at 129°; for its homologues, see A. **234**, 237. **Oxy-phenyl-phthalide** $C_6H_4\begin{cases}CH.C_6H_4.OH \\ COO\end{cases}$, m.p. 180°, is obtained from phthal-aldehydic acid, phenol, and sulphuric acid (73 per cent.) (B. **27**, 2632; **31**, 2790).

Benzo-hydrol-o_2-lactone-carboxylic acid $C_6H_4\begin{cases}CH—C_6H_4CO_2H \\ COO\end{cases}$, m.p. 202°, is produced on heating benzo-hydrol-tricarboxylic acid monolactone $(HOOCC_6H_4)_2C(OH)$, the reaction product of alkalies upon diphthalic acid (A. **242**, 233).

C. *Benzo-phenone-carboxylic acids* are formed (1) in the oxidation of the alkyl-diphenyl-methanes, alkyl-benzo-phenones, diphenyl-methane-carboxylic acids, and benzo-hydrol-carboxylic acids; (2) from

benzoyl chloride and benzoic anhydride with zinc chloride (B. **14,** 647); (3) from phthalic anhydride and benzene with aluminium chloride.

o-Benzoyl-benzoic acid $C_6H_5.CO.C_6H_4[2]CO_2H+H_2O$ melts, when anhydrous, at 127°. It is produced by oxidising o-tolyl-phenyl-methane, o-methyl-benzo-phenone, o-benzyl- and o-benzo-hydryl-benzoic acid. It can be prepared by method 3. Heated with phosphorus pentoxide, water is eliminated and anthraquinone is produced. Anthracene is produced when it is heated with zinc dust. With benzene and aluminium chloride ortho-benzoyl-benzoic acid yields phthalo-phenone; with phenol and stannic chloride, oxy-phthalo-phenone. When digested with acetic anhydride (B. **14,** 1865) it changes to:

Aceto-benzoyl-benzoic acid $C_6H_4\begin{cases}[1]C\langle^{C_6H_5}_{O.CO.CH_3}\\ [2]COO\end{cases}$, melting at 117° (compare aceto-lævulinic acid). The *oxime anhydride* melts at 162°. It is formed when hydroxylamine hydrochloride acts upon benzoyl-benzoic acid. At 130° it yields phthalanil (B. **26,** 1262, 1795). *Phenyl-lactazame* $C_6H_4\begin{cases}[1]C(C_6H_5):N\\ [2]CO\text{———}N.C_6H_5\end{cases}$, melting at 181° (compare lævulinic acid) (B. **18,** 805).

Chlorinated *benzoyl-benzoic acids* have been prepared from chlorinated phthalic anhydrides by the action of benzene and aluminium chloride (A. **238,** 338), and homologous *methyl-benzoyl-benzoic acids* from phthalic anhydride and toluol or other methyl benzols (B. **19,** R. 686; A. **311,** 178). Phthalic anhydride and dimethyl-aniline give **dimethyl-aniline-phthaloylic acid** $C_6H_4(COOH)COC_6H_4N(CH_3)_2$, m.p. 205° (A. **307,** 305). For transformation and substitution products of this acid, see C. 1901, I. 631, 944, etc.

m-Benzoyl-benzoic acid $C_6H_5.CO.C_6H_4[3]CO_2H$, melting at 161°, is made from iso-phthalic chloride, benzene, and aluminium chloride (A. **220,** 236; B. **13,** 320). **p-Benzoyl-benzoic acid,** melting at 194°, is prepared according to method 1 (B. **9,** 92).

Benzo-phenone-o_2-dicarboxylic acid $CO(C_6H_4[2]CO_2H)_2$ melts irregularly at 150°–200° with the elimination of water and a change to the dilactone. It is produced by oxidising benzo-hydrol-o_2-lactone-carboxylic acid with potassium permanganate. *Benzo-phenone-dicarboxylic dilactone* $\begin{matrix}COO\\ |\\ C_6H_4\end{matrix}\rangle C\langle\begin{matrix}OCO\\ |\\ C_6H_4\end{matrix}$, melting at 212°, is produced on boiling the aqueous solution of the acid, as well as by digesting its alcoholic solution with hydrochloric acid (A. **242,** 246).

o, p- and **p_2-Benzo-phenone-dicarboxylic acid,** m.p. 235° and above 360° respectively (A. **309,** 98; **311,** 96). **Phthaloyl-salicylic acid** $COOHC_6H_4COC_6H_3(OH)COOH$, m.p. 244°, from salicylic methyl ester, phthalyl chloride, and $AlCl_3$ (A. **303,** 280).

Benzoyl-phthalic acid $C_6H_5CO.C_6H_3[2,3](COOH)_2$, from hemimellitic anhydride, benzene, and Al_2Cl_6, melts at 183° with the formation of an anhydride (A. **290,** 217). Concentrated sulphuric acid converts it into anthraquinone-carboxylic acid.

1, 3, 4-Benzoyl-phthalic acid, m.p. 189°, is obtained by the oxidation of o-xyloyl-benzoic acid (A. **312,** 99).

Benzyl-diphenyls $C_6H_5.CH_2.C_6H_4.C_6H_5$ are formed from diphenyl,

benzyl chloride, and zinc dust. **p-Benzyl-diphenyl** melts at 85° and boils at 285° (100 mm.). **Iso-benzyl-diphenyl** melts at 54° and boils at 283°–287° (110 mm.) (B. **14**, 2242).

p-Phenyl-benzyl-o-benzoic acid $C_6H_5[4]C_6H_4[1]CH_2[2]C_6H_4[1]CO_2H$ melts at 184°, and **p-phenyl-benzo-hydryl-o-benzoic acid** $C_6H_5[4]C_6H_4[1]CH(OH).C_6H_4[2]CO_2H$ melts at 204°. Both are produced in the reduction of **p-phenyl-benzoyl-o-benzoic acid** $C_6H_5[4]C_6H_4[1]CO[2]C_6H_4[1]CO_2H$, melting at 225°, which results from the action of aluminium chloride upon a ligroïn solution of diphenyl and phthalic anhydride (A. **257**, 96; *J. pr. Ch.* 2, **41**, 149).

Dibenzyl-benzenes.—The second benzyl nucleus can be introduced into benzene and its homologues, containing replaceable hydrogen atoms attached to the nucleus, by the same reactions which were employed in introducing the first benzyl nucleus—*i.e.* by the action of zinc dust (B. **9**, 31) or aluminium chloride upon a solution of the benzyl chloride in the hydrocarbons, and by the action of sulphuric acid upon benzene and methylal (B. **6**, 221; **37**, 1467). **α- and β-Dibenzyl-benzol** melt at 86° and 78°.

Bis-amido-benzyl-resorcin $(NH_2C_6H_4.CH_2)_2C_6H_2(OH)_2$, m.p. 213°, is formed as a by-product of the condensation of p-amido-benzyl alcohol with resorcin by hot dilute sulphuric acid (C. 1903, I. 288).

o_2-Dibenzo-hydryl-benzol $C_6H_4(CHOHC_6H_5)_2$, m.p. 120°, from o_2-dibenzoyl-benzol by reduction with sodium amalgam. By the action of mineral acids it easily passes into **sym. diphenyl-phthalane** $C_6H_4\begin{cases}CH{-}C_6H_5\\ \quad\ O\\ CH{-}C_6H_5\end{cases}$, m.p. 96°, with expulsion of H_2O. This is also obtained synthetically from the result of the action of C_6H_5MgBr upon phenol phthalide by rejection of water and reduction (C. 1905, II. 137).

o_2-, m_2-, and **p_2-Dibenzoyl-benzols** $C_6H_4\langle^{CO.C_6H_5}_{CO.C_6H_5}$, **phthalo-phenones,** phenylene-diphenyl ketones, m.p. 146°, 100°, and 160° respectively. The ortho- and para-derivatives are produced by the oxidation of the corresponding dibenzyl-benzenes (B. **9**, 31).

The *meta-* and *para-*compounds may be obtained from meta- and para-phthalyl chlorides with benzene and $AlCl_3$ (B. **18**, 320), whereas the so-called ortho-phthalyl chloride yields diphenyl-phthalide.

1-Amido-2, 4-dibenzoyl-benzol $C_6H_3[1]NH_2[2, 4](COC_6H_5)_2$, m.p. 138°, is obtained in the form of its benzoyl compound, m.p. 156°, by heating one molecule aniline with three molecules benzoyl chloride by intramolecular atomic displacement by way of dibenzoyl amido-benzo-phenone (C. 1905, I. 444).

Dibenzoyl-mesitylene $(CH_3)_3[1, 3, 5]C_6H(COC_6H_5)_2$, m.p. 117°, from mesitylene, two molecules benzoyl chloride, and $AlCl_3$, gives on oxidation **sym.** and **unsym. dibenzoyl-mesitylenic acid** $(C_6H_5CO)_2C_6H(CH_3)_2COOH$, m.p. 222° and 174°, **sym.** and **unsym. dibenzoyl-uvitinic acid** $(C_6H_5CO)_2C_6H(CH_3)(COOH)_2$, m.p. 262° and 211°, and finally **dibenzoyl-trimesinic acid** $(C_6H_5CO)_2C_6H(COOH)_3$, m.p. 250° (C. 1902, II. 1181).

III. Triphenyl-methane Group.

Triphenyl-methane, tolyl-diphenyl-methane, and ditolyl-phenyl-methane are the parent hydrocarbons from which originate the *ros-*

anilin dyes, the *malachite greens*, the *aurins*, and *phthaleins*, from which they can be obtained by various transposition and decomposition reactions. However, in no one of these instances do they constitute the foundation material for the technical preparation of the above-mentioned dyes.

1. *Hydrocarbons.*—The methods of forming the triphenyl-methane hydrocarbons are evident if one simply makes more general those methods which are employed in the preparation of triphenyl-methane.

Triphenyl-methane $CH(C_6H_5)_3$, m.p. 92° and b.p. 358°. It is produced :

(1) By the action of benzal chloride upon mercury diphenyl (1872, Kekulé and Franchimont, B. **5**, 907).

(2) From benzal chloride or benzo-trichloride and benzene (*a*) by the action of zinc dust, (*b*) with aluminium chloride (B. **12**, 976, 1468; **14**, 1526).

(3) From chloroform or carbon tetrachloride and benzene, aided by $AlCl_3$ (A. **194**, 254 ; **227**, 107 ; B. **18**, R. 327).

(4) From chloroform or benzal chloride and phenyl-magnesium bromide (C. 1906, II. 1262).

(5) By the action of P_2O_5 at 140° (B. **7**, 1204) upon benzo-hydrol and benzene.

(6) From triphenyl-carbinol or its bromide by reduction (B. **37**, 616, 1249 ; **44**, 441).

(7) By the action of nitrous acid and alcohol upon di- and tri-amido-triphenyl-methane sulphate (A. **206**, 152).

The latter reaction is of the greatest fundamental importance in demonstrating the connection between p-rosanilin and triphenyl-methane.

Triphenyl-methane crystallised from benzene contains *benzene of crystallisation* $CH(C_6H_5)_3+C_6H_6$, m.p. 75° ; and from thiophene, pyrrol, and aniline it separates with *thiophene* (*pyrrol*, or *aniline*) *of crystallisation* $CH(C_6H_5)_3+C_4H_4S$ (B. **26**, 853). It is oxidised to triphenyl-carbinol, and is reduced with hydrogen and finely divided nickel at 220° to tricyclo-hexyl-methane, b.p.$_{20}$ 140° (C. 1909, I. 173), and by hydriodic acid, and some red phosphorus at 280°, to benzene and toluol. When heated with potassium, it yields *triphenyl-methane-potassium* $(C_6H_5)_3CK$, which combines with CO_2 to potassium-triphenyl acetate.

o-, m-, p-Methyl-triphenyl-methane, *diphenyl-o-, m-, p-tolyl-methane* $(C_6H_5)_3CH.C_6H_4.CH_3$, melt at 83°, 62°, and 71° ; from the carbinols by reduction. The m-compound was obtained by the action of nitrous acid and alcohol upon leucaniline sulphate (A. **194**, 282 ; cp. B. **37**, 1245). The p-tolyl-diphenyl-methane is easily prepared from benzo-hydrol and toluol, with tin tetrachloride (B. **37**, 659).

Diphenyl-o-, m-, p-xylyl-methanes melt at 68°, 61°, and 92° ; they have been obtained from benzo-hydrols with o-, m-, and p-xylol by means of P_2O_5 (B. **16**, 2360).

Nitro-substitution Products.—**m-** and **p-Nitro-diphenyl-methane** $NO_2.C_6H_4.CH(C_6H_5)_2$, m.p. 90° and 93°, are obtained from m- and p-nitro-benzaldehyde, benzene, and zinc chloride (B. **21**, 188 ; **23**, 1622).

When triphenyl-methane is dissolved in fuming nitric acid (sp. gr. 1·5) it forms **p-trinitro-phenyl-methane** $CH(C_6H_4[4]NO_2)_3$, which melts at 206°. Sodium alcoholate converts the nitro-compound into

a deep violet-coloured sodium salt. It dissolves in alcoholic potassium hydroxide with a violet colour (B. **21,** 2476). On further nitration with nitro-sulphuric acid we obtain **o_3p_3-hexanitro-triphenyl-methane** $CH[C_6H_4(NO_2)_2]_3$, m.p. 260° with decomposition, which, on reduction with alcoholic Am sulphide, yields trinitro-triamido-triphenyl-methane (B. **36,** 2779).

p-Trinitro-diphenyl-m-tolyl-methane $(NO_2[4]C_6H_4)_2CH.C_6H_3[4]NO_2[3]CH_3$.

Amido-derivatives are produced (1) by the reduction of the corresponding nitro-bodies; (2) by reduction of the corresponding amido-carbinols, the colour-bases of the malachite green and rosanilin groups, as the *leuco-derivatives* of which they are frequently designated; (3) by the condensation of benzo-hydrol or benzaldehyde and aniline hydrochloride, or dimethyl-aniline hydrochloride, with P_2O_5 or $ZnCl_2$. (4) Mixed diamido-triphenyl-methanes are also obtained as follows:— Benzylidene-anilines unite with anilines to form amido-benzo-hydril-phenylamines: the latter, with aromatic amine salts, yield diamido-triphenyl-methanes (C. 1900, II. 548):

$$C_6H_5CH:NC_6H_5 \xrightarrow{C_6H_5NH_2} C_6H_5CH\begin{matrix}C_6H_4NH_2\\NHC_6H_5\end{matrix} \xrightarrow[HCl]{C_7H_7NH_2} C_6H_5CH\begin{matrix}C_6H_4NH_2\\C_7H_6NH_2\end{matrix}.$$

When oxidised with chloranile, or PbO_2 and hydrochloric acid, etc., their salts change to those of the colour-bases to which malachite green and rosanilin belong; they are derived from triphenyl-carbinol.

o-Amino-triphenyl-methane $(C_6H_5)_2CHC_6H_4[2]NH_2$, m.p. 129°, from the corresponding amino-carbinol by reduction with zinc dust and glacial acetic acid (B. **37,** 3198).

m-Amino-triphenyl-methane $(C_6H_5)_2CHC_6H_4[3]NH_2$, melting at 120°, is obtained from m-nitro-triphenyl-methane (B. **21,** 189).

p-Amino-triphenyl-methane, melting at 84°, is formed (1) from p-nitro-triphenyl-methane (B. **28,** 1623); (2) from benzo-hydrol, aniline hydrochloride, and zinc chloride (A. **206,** 155); (3) from phenyl-benzo-hydrylamine by heating with aniline chlorohydrate (B. **38,** 1768).

p-Dimethyl-amido-triphenyl-methane $(C_6H_5)_2CH.C_6H_4[4]N(CH_3)_2$, melting at 132°, is formed from benzo-phenone chloride and dimethyl-aniline, as well as from benzo-hydrol and dimethyl-aniline with P_2O_5 (A. **206,** 113), as well as from benzo-phenone, dimethyl-aniline, and zinc chloride (A. **242,** 341). **p-Acetamido-triphenyl-methane** melts at 176° (B. **24,** 728).

p_2-Diamido-triphenyl-methane $C_6H_5.CH(C_6H_4[4]NH_2)_2$, melting at 139°, + C_6H_6 at 106°, the parent substance of *malachite green,* is obtained (1) from benzal chloride and aniline with zinc dust; (2) from benzaldehyde with aniline hydrochloride on heating with zinc chloride to 120° (B. **15,** 676), or by boiling benzaldehyde with aniline and hydrochloric acid (B. **18,** R. 334); (3) by reducing diamino-triphenyl-carbinol chloride with zinc dust. The diacetyl derivative, m.p. 234°, s sparingly soluble.

p_2-Tetramethyl-diamino-triphenyl-methane $C_6H_5.CH[C_6H_4[4]N(CH_3)_2]_2$, *leuco-malachite green,* is dimorphous, and crystallises in flakes, melting at 93°–94°, or in needles, which melt at 102°. The first modification is obtained pure by crystallisation from alcohol, the second from benzene. It is obtained by methylating p_2-diamido-triphenyl-

methane, as well as by the action of benzaldehyde upon dimethyl-aniline. Technically, it is made by the condensation of benzaldehyde and dimethyl-aniline with hydrochloric or sulphuric acid (formerly zinc chloride or oxalic acid). By oxidation it becomes p_2-tetramethyl-diamido-triphenyl-carbinol, the basis of malachite green.

By heating with BrCN, leuco-malachite green yields **dimethyl-dicyano-diamido-triphenyl-methane** $[CH_3N(CN)C_6H_4]_2CHC_6H_5$, m.p. 163°, which, on saponification with HCl, yields **p_2-dimethyl-diamino-triphenyl-methane** $(CH_3NH.C_6H_4)_2CHC_6H_5$, m.p. 104° (B. **37,** 637).

o- and **m-Nitro-p_2-diamido-triphenyl-methane** are produced in the condensation of o- and m-nitro-benzaldehyde with aniline sulphate by means of zinc chloride. The m-body melts at 136° (B. **18,** 671; **16,** 1305).

p-Nitro-p_2-diamino-triphenyl-methane is obtained from p-nitro-benzaldehyde, just as the o- and m-compounds are prepared. See p-Leucaniline (B. **25,** 676).

Benzaldehyde and the nitro-benzaldehydes condense with o- and p-toluidin, just as they do with aniline and dimethyl-aniline (B. **18,** 2094), whereas m-toluidin and m-derivatives of aniline only react readily if the amido-group is methylated (B. **20,** 1563).

Triamino-triphenyl-methanes result from the reduction of the nitro- and nitro-amido-triphenyl-methanes and of the triamido-triphenyl-carbinols. The latter are the rosanilin bases if the three amido-groups occur in the p-position with reference to the C(OH) group. Their reduction products are also called leucanilines. These are white precipitates, and when oxidised yield the carbinols:

o, p_2-Triamido-triphenyl-methane, or *o-leucaniline*,
and m, p_2-Triamido-triphenyl-methane, or *pseudo-leucaniline*,
and p_3-Triamido-triphenyl-methane, or *para-leucaniline*,

which, upon oxidation, yield dyestuffs. That from the o-body is brown in colour, that from the m-body is violet, while that from the p-compound is *para-rosanilin*. p-Triamido-triphenyl-methane is also produced in the condensation of p-amino-benzaldehyde and aniline with zinc chloride; its tris-diazo-chloride $CH(C_6H_4.N_2Cl)_3$, when boiled with alcohol, forms triphenyl-amine.

p_3-Triamido-diphenyl-m-tolyl-methane, *leucaniline* $(NH_2[4]C_6H_4)_2CH.C_6H_3[4](CH_3).NH_2[3]$, is the leuco-compound corresponding to the chief constituent of rosanilin obtained by the reduction of trinitro-diphenyl-meta-tolyl-methane, and is also made by digesting the fuchsine salts with ammonium sulphide, or zinc dust and hydrochloric acid. By diazotising, and replacing the diazo-groups by hydrogen (best effected by dissolving in concentrated sulphuric acid, conducting nitrous acid into the same, and boiling with alcohol), leucaniline is changed into diphenyl-m-tolyl-methane.

2. **Carbinols** are formed (1) by oxidising the triphenyl-methane hydrocarbons, and their nitro- and amido-compounds, and by many synthetic methods; (2) from aryl-magnesium haloids, (*a*) with aromatic carboxylic esters or benzo-phenones (B. **35,** 3024; **36,** 406; **37,** 663, 990):

$$\left.\begin{matrix} C_6H_5COOCH_3 + 2C_6H_5MgBr \\ C_6H_5COC_6H_5 + C_6H_5MgBr \end{matrix}\right\rangle \longrightarrow (C_6H_5)_3C(OH);$$

(*b*) with other products, by the action of CO_2, COS, $COCl_2$, ClCOOR (B. **36**, 1010, 3005, 3087, 3236) :

$$3C_6H_5MgBr \xrightarrow{CO_2} (C_6H_5)_3C(OH).$$

(3) from triaryl-acetic acids by rejection of CO on treating with concentrated H_2SO_4 (B. **37**, 655) :

$$(C_6H_5)_2C(C_6H_4CH_3)COOH \xrightarrow{-CO} (C_6H_5)_2C(C_6H_4.CH_3)OH.$$

Triphenyl-carbinol $(C_6H_5)_3C.OH$, m.p. 163°, b.p. above 360°. **o-, m-,** and **p-Tolyl-diphenyl-carbinol** $(C_6H_5)_2(C_6H_4.CH_3)C.OH$, m.p. 98°, 65°, and 74° (B. **37**, 656, 992, 1245). **Tri-p-tolyl-carbinol** $(CH_3C_6H_4)_3.C.OH$, m.p. 96° (B. **37**, 3153).

Diphenyl-mono-biphenyl-carbinol $(C_6H_5)_2C(OH).C_6H_4.C_6H_5$, m.p. 136° ; **phenyl-di-biphenyl-carbinol** $(C_6H_5.C_6H_4)_2C(OH)C_6H_5$, m.p. 151° ; **tri-biphenyl-carbinol** $(C_6H_5.C_6H_4)_3C.OH$, m.p. 208°, see A. **368**, 298.

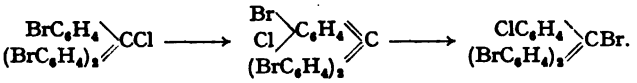
The OH group of triphenyl-carbinol and its homologues is very reactive. Triphenyl-carbinol is easily etherified by alcohols, forming triphenyl-carbinol-methyl ether $(C_6H_5)_3COCH_3$, m.p. 82°. The ethers are easily saponified with acids. With bisulphites we obtain salts of triphenyl-methyl-sulphonic acids $(C_6H_5)_3C.SO_3Na$; with aniline we obtain triphenyl-carbinol-aniline, while aniline chlorohydrate yields p-amido-tetraphenyl-methane, and tetraphenyl-methane derivatives are similarly formed with phenol and anisol. With sulphuric acid the carbinols form coloured unstable acid sulphates, whose stability is increased with the introduction of halogen or methoxylene into the benzene nuclei of the carbinols (B. **38**, 1156). Especially characteristic are the easily crystallised perchlorates of the triphenyl-carbinols, which are also intensely coloured (B. **43**, 183). With pyridin and quinolin also, triphenyl-carbinol produces saline compounds (B. **35**, 4007).

Triphenyl-chloro-methane, *triphenyl-carbinol chloride* $(C_6H_5)_3CCl$, m.p. 111°, is formed from carbinol by treatment with hydrochloric acid in glacial acetic acid, with PCl_5 or with acetyl chloride (B. **36**, 384, 3924) ; also on heating triphenyl-acetic chloride with concentrated sulphuric acid, CO being eliminated. It is formed synthetically from benzene and CCl_4 with aluminium chloride (cp. C. 1902, I. 463). **Triphenyl-bromo-methane,** from triphenyl-methane in CS_2 with bromine in sunlight (A. **227**, 110), or from the carbinol with glacial acetic hydrobromic acid (B. **42**, 3024). **Triphenyl-iodo-methane,** m.p. 132°, by the action of iodine in CS_2 upon a solution of triphenyl-methyl. Its solutions, when exposed to the oxygen of the air, eliminate iodine, and form triphenyl-methyl peroxide. With excess of halogen the triphenyl-halogen-methanes unite to form well-crystallised perhaloids $(C_6H_5)_3CBr.Br_5$, $(C_6H_5)_3CBr.I_5$, $(C_6H_5)_3CI.I_5$, etc. (B. **35**, 1831).

The halogen is bound up in the triphenyl-halogen-methanes remarkably loosely. In many respects they behave like metallic salts, their solutions in sulphurous acid, pyridin, and acetone conducting the electric current (B. **43**, 336). In the electrolysis of triphenyl-bromo-methane in a solution of SO_2, it is split up, just like a metallic salt, into bromine, and the radicle triphenyl-methyl $(C_6H_5)_3C$, which is partly transformed into the dimeric hexaphenyl-ethane (A. **372**, 11). On

boiling with water the triphenyl-halogen-methanes are transposed into triphenyl-carbinol. On treatment with silver acetate we obtain triphenyl-carbinol acetate $(C_6H_5)_3COCOCH_3$, m.p. 88° (B. **36,** 3926); with potassium cyanide we obtain triphenyl-aceto-nitrile.

Triphenyl-chloro-methane is colourless in the solid state, and dissolves in SO_2 with a yellow colour, being probably transposed into the quinoid form $(C_6H_5)_2C : C_6H_4\langle{}^{H}_{Cl}$. In agreement with this view, the p_3 - tribromo - triphenyl - chloro - methane can be transformed, by crystallisation, from sulphurous acid into the isomeric, and less soluble, p_3-monochloro-dibromo-triphenyl-bromo-methane with exchange of a bromine and chlorine atom, the following bases being passed through (B. **42,** 406) :



With metallic chlorides, such as $AlCl_3$, $ZnCl_3$, $SnCl_4$, etc., triphenyl-chloro-methane yields intensely coloured double compounds, which, like the carbinol sulphates and perchlorates mentioned above, probably belong to the quinoid type. With magnesium and ether, it forms the very unstable *triphenyl-methyl-magnesium chloride* $(C_6H_5)_3CMgCl$. By the action of zinc, or molecular silver, or copper, upon the benzene solution of triphenyl-chloro-methane with the exclusion of air, we obtain triphenyl-methyl and hexaphenyl-ethane respectively. By heating above 280° triphenyl-chloro- and bromo-methane are condensed to *diphenylene-phenyl-methane* $(C_6H_4)_2CHC_6H_5$.

Triphenyl-methyl-amine, *triphenyl-carbinol-amine* $(C_6H_5)_3C.NH_2$, m.p. 103°, is prepared by conducting dry ammonia gas into a benzene solution of triphenyl-carbinol bromide, chloride, or iodide (B. **17,** 442, 741 ; **35,** 1827).

Triphenyl-methyl-aniline $(C_6H_5)_3C.NHC_6H_5$, m.p. 144°, is also formed from triphenyl-carbinol by heating with aniline in glacial acetic acid (B. **17,** 703, 746 ; **35,** 3016). A derivative of triphenyl-methyl-amine is the so-called **diphenyl-benzyl-sultame** $C_6H_4\{{}^{[1]C(C_6H_5)_2}_{[2]SO_2}\rangle NH$, m.p. 210°, formed besides phenyl-benzal-sultime in the condensation of pseudo-saccharin chloride with benzene and $AlCl_3$ (B. **29,** 2296).

Triphenyl-methyl-hydrazin $(C_6H_5)_3C.NHNH_2$, chlorohydrate, m.p. 133°, is formed, besides hydrazo-triphenyl-methane, in the action of hydrazin hydrate upon triphenyl-chloro-methane. With HNO_2 it yields **triphenyl-methyl-azide** $(C_6H_5)_3CN\langle{}^{N}_{N}$, m.p. 64°, a remarkably stable ester of hydrogen nitride (B. **42,** 3024).

Triphenyl-methane-hydrazo-benzol $(C_6H_5)_3CNHNHC_6H_5$, m.p. 137°, from triphenyl-carbinol chloride or bromide with phenyl-hydrazin. It is oxidised by HNO_2 to **triphenyl-methane-azo-benzol** $(C_6H_5)_3CN : NC_6H_5$, m.p. 114° (B. **36,** 1088).

Hydrazo-triphenyl-methane $(C_6H_5)_3C.NHNH.C(C_6H_5)_3$, m.p. 209°, from triphenyl-chloro-methane and hydrazin hydrate. By oxidation with sodium hypo-bromite it decomposes by way of the very unstable azo-triphenyl-methane into nitrogen and triphenyl-methyl. Bromine or

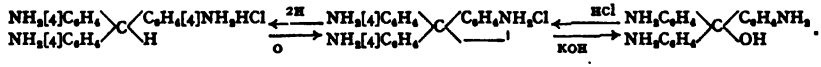
iodine converts it into triphenyl-bromo- and iodo-methane respectively, or into the perhaloids (B. **42,** 3020).

m- and **p-Bromo-triphenyl-carbinol,** m.p. 67° and 114°, from m- and p-bromo-benzoic ester and C_6H_5MgBr. **p-Trichloro-triphenyl-carbinol,** m.p. 99°, from p-chloro-iodo-benzol, p-chloro-benzoic ester, and magnesium. **p-Tri-iodo-triphenyl-carbinol,** m.p. 163°, from the tri-diazonium sulphate of p-rosanilin with iodo-potassium iodide (B. **38,** 585).

m- and **p-Nitro-triphenyl-carbinol** $(C_6H_5)_2C(OH)C_6H_4NO_2$, m.p. 75° and 98°; the p-compound is obtained pure from its chloride, the condensation product of p-nitro-benzo-phenone chloride with benzene and $AlCl_3$ (B. **21,** 190; **37,** 604).

p_3-Trinitro-phenyl-carbinol $(NO_2[4]C_6H_4)_3.C.OH$, m.p. 171°, is prepared from p_3-trinitro-phenyl-methane by the action of chromic acid in glacial acetic acid. It yields p-rosanilin upon reduction.

Amido-triphenyl-carbinols.—p_2-Diamido-triphenyl-carbinol and p_3-triamido-carbinols, of this class, deserve special consideration. p_2-Tetramethyl-diamido-triphenyl-carbinol is the basis of malachite green, and p_3-triamido-triphenyl-carbinol that of p-rosanilin. The free amido-carbinols are colourless. In contact with acids water is eliminated and colour salts result. These are also formed by the direct oxidation of the salts of the leuco-compounds, and pass into the latter upon reduction. Thus p-leucaniline hydrochloride (1) yields, upon oxidation, p-rosanilin chloride, from which colourless p_3-triamido-triphenyl-carbinol is separated by bases; hydrochloric acid converts this compound again into p-rosanilin chloride:



Only these mono-, di-, and triphenyl-carbinols are capable of forming coloured salts with expulsion of water, which contain at least one amido-group in the p-position. Dyestuffs are only formed if two p-amido-groups are present.

With a careful transposition of the dye salts with soda solution, the first phase is the production of more or less unstable methylene-quinone-imide $Ar_4C : C_6H_4 : NR$, or $Ar_2C : C_6H_4 : NR_2OH$ (cp. Methylene quinones), and in a second phase they either attach or transpose water and form amino-carbinols.

These reactions, occurring even in the simplest p-amino-carbinols, are similarly repeated in the p-oxy-triphenyl-carbinols. According to this we may regard diphenyl-quino-methane as the foundation substance for the dyestuffs of the triphenyl-methane series, which therefore can be termed fuchsone on account of the most important dye (B. **37,** 2848):

$(C_6H_5)_2C : C_6H_4 : O$ $(C_6H_5)_2C : C_6H_4 : NH$ $(C_6H_5)_2C : C_6H_4 : NH_2Cl$
Fuchsone [Fuchsone-imine] Fuchsone-imonium chloride.

p-Amino-triphenyl-carbinol $HO.C(C_6H_5)_2.C_6H_4NH_2$, from its acetyl derivative formed by oxidation from acetamido-triphenyl-methane with PbO_2. With HCl it first forms the feebly coloured or colourless salts $HO.C(C_6H_5)_2C_6H_4NH_2.HCl$ and $ClC(C_6H_5)_2C_6H_4NH_2.HCl$,

which, on heating, expel H_2O or HCl, and form the strongly coloured salts of the bases free from oxygen. The latter, anhydro-p-amido-triphenyl-carbinol (*fuchsone-imine*), is dimolecular and colourless in the free state $[(C_6H_5)_2C.C_6H_4 : NH]_2$. Its salts are also obtained from the condensation products of p-amido-benzo-phenone with phenyl-magnesium bromide (B. **37**, 597).

p-Anilino-triphenyl-carbinol, colourless, is formed from the anhydro-base, **diphenyl-methylene-quinone-phenyl-imine,** *fuchsone-anile* (see above) $(C_6H_5)_2C{:}\ C_6H_4 : NC_6H_5$, red prisms, melting at 133°–138°, by addition of water. For forming the latter, diphenyl-p-anisile-carbinol-anilide $(C_6H_5)_2C(NHC_6H_5)C_6H_4OCH_3$, with organic acids like benzoic acid (B. **37**, 608).

p-Dimethyl-amino-triphenyl-carbinol $(CH_3)_2N.C_6H_4C(OH)(C_6H_5)_2$, m.p. 93°, from p-dimethyl-amino-phenyl-magnesium bromide with benzo-phenone, or benzo-phenone chloride, dimethyl-aniline, and $ZnCl_2$ (B. **36**, 4296 ; **37**, 2857).

o-Amino-triphenyl-carbinol, m.p. 121°, from anthranilic ester and C_6H_5MgBr. On prolonged heating it expels water and forms phenyl-acridin. The chlorohydrate of carbinol chloride, on treatment with pyridin, gives an anhydro-compound $(C_{19}H_{15}N)_2$ analogous to the p-compound, m.p. 250° with decomposition (B. **37**, 3191).

m-Amino-triphenyl-carbinol, m.p. 155° (B. **21**, 190).

p_2-Diamino-triphenyl-carbinol $(NH_2C_6H_4)_2C(OH)C_6H_5$, colourless crystals, best obtained by oxidising the diaceto-diamino-triphenyl-methane with MnO_4, saponification and purification over methyl ether, m.p. 161°–163°. On heating it splits off water and passes into the unstable methylene-quinone-imine base (amino-fuchsone-imine), the salts of which are purple-violet dyestuffs, resembling fuchsine (B. **37**, 2859).

p_2-Dimethyl-diamino-triphenyl-carbinol $(CH_3NH.C_6H_4)_2C(OH)C_6H_5$, m.p. 95°, is formed by saponifying the *cyanated carbinol* $[CH_3N(CN)C_6H_4]_2C(OH)C_6H_5$, generated from the corresponding triphenyl-methane derivative by oxidation with permanganate in acetone solution (B. **37**, 641).

p_2-Tetramethyl-diamido-triphenyl-carbinol $C_6H_5.C(OH)[C_6H_4[4]N(CH_3)_2]_2$, melting at 132°, crystallises from benzene in colourless forms. It is obtained from its salts (malachite green) by precipitation with the alkalies and by oxidising an alcoholic solution of p_2-tetramethyl-diamido-triphenyl-methane with chloranile (A. **206**, 130), and from p-dimethyl-amido-phenyl-magnesium bromide with benzoic acid ester (B. **36**, 4296).

Methyl ether $C_6H_5C(OCH_3)[C_6H_4N(CH_3)_2]_2$, m.p. 151° (B. **33**, 3356 ; **37**, 2867). **Iodo-methylate** $C_6H_5C(OCH_3)[C_6H_4N(CH_3)_3I]_2+2H_2O$ is obtained by heating p_2-diamido-triphenyl-carbinol and p_2-tetramethyl-diamido-triphenyl-carbinol with methyl iodide and methyl alcohol.

The free base yields almost colourless solutions with acids in the cold ; upon standing, and more rapidly on heating, the solution acquires a green colour and then contains the green salts—*malachite greens*—of the anhydro-base of the carbinol (B. **12**, 2348 ; **33**, 298).

Malachite green, *bitter almond oil green* $C_6H_5.C\begin{cases}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2Cl\end{cases}$, the hydrochloride of the anhydro-base, is produced when zinc chloride

acts upon a mixture of benzo-trichloride and dimethyl-aniline, or upon a mixture of benzoyl chloride and dimethyl-aniline (A. **206**, 137).

Technically, leuco-malachite green is first prepared, and its hydrochloride then oxidised with lead peroxide. While benzoic acid cannot be condensed with dimethyl-aniline, ortho-methylated benzoic acids with tertiary anilines give green dyes corresponding to malachite green by a clean reaction (C. 1899, I. 1089).

Malachite green, characterised by its strong colouring power, is usually supplied commercially in the form of its *zinc chloride double salt* $(C_{23}H_{25}N_2Cl)_2.2ZnCl_2+2H_2O$, or its *oxalate* $(C_{23}H_{25}N_2)_23C_2O_4H_2$.

History.—Malachite green, or *bitter almond oil green*, was obtained in 1877 by O. Fischer, in the oxidation of p_2-tetramethyl-diamido-triphenyl-methane. He obtained the latter compound by condensing benzaldehyde with dimethyl-aniline. Doebner (1878) showed how malachite green could be prepared from benzo-trichloride and dimethyl-aniline.

Brilliant green, *solid green, new Victoria green,* is the tetra-ethyl derivative, corresponding to malachite green, which is made from diethyl-aniline and benzaldehyde (B. **14**, 2521). The colour is more yellow-tinted than that of malachite green.

Acid green is a dye obtained from benzaldehyde and benzyl-ethyl aniline by condensation, oxidation, and sulphonation. The sulpho-groups are in the benzyl residue (B. **22**, 588).

Nitro-malachite greens have been prepared with o-, m-, and p-nitro-benzaldehydes and dimethyl-aniline as the foundation substances (B. **15**, 682). **o-Amino-malachite green** is a blue dye. The base is formed from the urethane of *o-amino-leuco-malachite green* $COOC_2H_5.NH[2]C_6H_4CH[C_6H_4:N(CH_3)_2]_2$ by oxidation and saponification (B. **36**, 2776). Further substituted malachite greens, see B. **39**, 2041.

o, p'-, m, p'-, o, m'- and **m, m'-Tetramethyl-diamino-triphenyl-carbinol,** m.p. 170°, 140°, 184°, and 129° respectively, have been obtained from the corresponding amido-benzo-phenones by transformation with C_6H_5MgBr or $(CH_3)_2NC_6H_4Mg$ (A. **354**, 195).

Triamido-triphenyl-carbinols.—*p_2-Triamido-triphenyl-carbinol, p_3-triamido-diphenyl-m-tolyl-carbinol,* and their methyl, ethyl, benzyl, and phenyl derivatives, are of the highest importance in the coal-tar colour industry. Their salts, with one equivalent of acid, hydrochloric or acetic, constitute the group of rosanilin dyes in the more restricted sense. Like malachite green, the rosanilin dye substances are free from carbinol oxygen, as the salt formation is accompanied by an intramolecular anhydride formation. The carbinols separated from these salts by alkalies are colourless, but turn red on exposure to the air. Careful treatment of p-rosanilin with sodium hydroxide yields first a polymeride of the methylene-quinone-imine base (of *p_2-diamino-fuchsone-imine,* free from oxygen) in feebly tinted needles. On heating p_3-triamino-triphenyl-carbinol in a current of hydrogen to 200°, a base, also free from oxygen, forms as a red amorphous mass, which, with acids, regenerates para-rosanilin quantitatively (B. **37**, 1183, 2867). This process may be represented as follows :

$$(NH_2C_6H_4)_2C(OH)C_6H_4NH_2 \longleftrightarrow [(NH_2C_6H_4)_2C:C_6H_4:NH]x \longleftrightarrow (NH_2C_6H_4)_2C:C_6H_4:NH_2Cl$$

Fuchsine is the dyestuff produced in the oxidation of a mixture of

aniline, o-toluidin, and p-toluidin. It is the so-called *red oil*. **Rosanilin** is the chief ingredient of fuchsine. It is the hydrochloride or acetate of *anhydro-p_3-triamido-diphenyl-m-tolyl-carbinol* $C_{20}H_{19}N_3.HCl+4H_2O$ or $C_{20}H_{19}N_3.C_2H_4O_2$. The mon-acid salts combine with two additional equivalents of acid, forming yellowish-brown coloured salts, which water decomposes into the stable *mon-acid* salts with intense colours. These are applied as dyes. They are mostly readily soluble in water and alcohol, and crystallise in metallic greenish crystals. Their solutions are carmine-red in colour, and stain animal tissue directly violet-red, while vegetable fibre (cotton) must first be mordanted (tannin).

The mono- and tri-acid salts of rosanilin, on taking up four molecules HCl, NH_3, or H_2O, become colourless additive compounds, which easily split off the added substances and reproduce the dyes (*A. Chim. Phys.* 8, **7**, 195).

Fuchsine combines with sulphurous acid, forming the readily soluble, colourless *fuchsine-sulphurous acid*.

Aldehydes impart a red colour to this solution, which serves as a reagent for them.

Oxidants used with *red oil* are stannic chloride (Verguin, 1859), mercurous and mercuric nitrates, arsenic acid at 180°–200° (Medloc, Nicholson, Girard, and de Laire, 1860); nitro-benzol with a little ferrous chloride or ammonium vanadate at 180°–190°, when the half of the red oil is applied as hydrochloride (Coupier, 1869; cp. B. **6**, 25, 423, 1072).

In the *arsenic acid method* the fuchsine is obtained in the form of arsenites, which are then converted into the chlorohydrate or acetate, and obtained free from arsenious acid by recrystallisation.

The *nitro-benzol method* yields immediately a fuchsine which is not poisonous. The nitro-benzol only acts as an oxidant, without entering into the fuchsine formation at all.

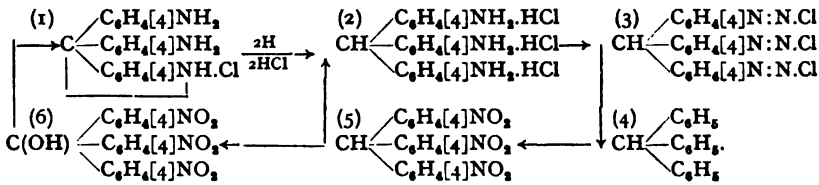
Fuchsine is not formed either from aniline or from p-toluidin, or from o-toluidin alone. Even a mixture of aniline with o-toluidin is not oxidised to fuchsine. However, not only a mixture of aniline with o- and p-toluidin yields fuchsine, but in the oxidation of a mixture of aniline and p-toluidin a dye, with the properties of fuchsine, called para-rosanilin, is produced. This is also present in small amount in the fuchsine made from aniline and o- and p-toluidins; whereas the principal constituent of ordinary fuchsine consists of the next higher homologue of para-rosanilin, namely, rosanilin (B. **18**, 2204).

By-products in the Formation of Fuchsine.—The fuchsine solution contains, in addition to 34 per cent. of fuchsine, other violet and brown dyes: *mauvanilin*, *violanilin*, substances belonging probably to the indulins, and other less thoroughly investigated substances, as well as slight amounts of a yellow acridin dye, known as *phosphin* or *chrysanilin*.

History of the Recognition of the Constitution of Rosanilin and Pararosanilin.—A. W. Hofmann was the first person to engage in a scientific study of fuchsine. He began his investigations in the sixties, and was led, as a consequence, to present a formula for fuchsine and its fundamental dye-base. He became acquainted with numerous derivatives of fuchsine, especially the methyl and ethyl violet fuchsines. He assumed that the nitrogen atoms held together the radicles in the

fuchsine molecule. However, Kekulé (1867) argued for the possibility that the methyl groups of the toluidin molecules, necessary for the production of fuchsine, afforded the connection. K. Zulkowsky (1869) assumed the presence of three amido-groups in fuchsine, and considered it a derivative of a hydrocarbon with the formula $C_{18}H_{14}$. Gradually, however, the conviction grew that fuchsine sprang from a higher aromatic hydrocarbon. This idea had its basis or origin in the experiments of Wanklyn, Caro, Graebe, Dale, Schorlemmer, and others, which, in the main, established the relationship of fuchsine to rosolic acid. The "keystone to that extended series of experimental and speculative investigations" was the conversion (1878) of para-rosanilin, prepared by the oxidation of aniline and p-toluidin, into triphenyl-methane. This was the work of Emil and Otto Fischer. The hydrocarbon prepared by them from rosanilin, the chief constituent of fuchsine, proved to be diphenyl-m-tolyl-methane.

Triphenyl-methane (4) is formed in the decomposition of the tridiazo-sulphate of para-leucaniline with alcohol. In the diagram the formula of the tridiazo-chloride (3) of para-leucaniline (2) is used for the sake of simplicity. Concentrated nitric acid converts triphenyl-methane into p_3-trinitro-triphenyl-methane (5), which, upon reduction, yields p_3-triamido-triphenyl-methane or para-leucaniline (2). The latter, by oxidation, is converted into p_3-trinitro-triphenyl-carbinol (6). On oxidising para-leucaniline with arsenic acid, or by reducing p_3-trinitro-phenyl-carbinol with acetic acid and zinc dust, para-rosanilin (1) results. The following diagram illustrates this series of reactions, which were carried out, beginning with rosanilin itself (A. **194**, 242) :



Para-rosanilin is produced by oxidising a mixture of aniline and p-toluidin according to the arsenic acid or nitro-benzol method. The reaction may be imagined to proceed in that a molecule of p-toluidin is oxidised to p-amido-benzaldehyde; the latter then condenses with two molecules of aniline to para-leucaniline or p_3-triamido-triphenyl-methane, from which, finally, para-rosanilin results by oxidation.

When working with small quantities, the most convenient way of oxidising aniline and p-toluidin to para rosanilin consists in using mercuric chloride (B. **24**, 3552). An interesting formation of para-rosanilin is that of heating aniline with carbon tetrachloride to 230°, when the latter furnishes the linking carbon atom. The hydro-iodide of para-rosanilin results by using iodoform CHI_3.

Para-rosanilin is further formed by the reduction of p_3-trinitro-triphenyl-carbinol (see above); by heating γ_3-nitro-diamido-triphenyl-methane with ferrous chloride (B. **15**, 678); triamido-triphenyl-carbinol is also formed by moderated reduction of p-nitro-diamido-triphenyl-methane, inasmuch as the diamido-diphenyl-methane-phenyl-hydroxylamine $(C_6H_4NH_2)_2CH.C_6H_4.NHOH$, formed at first,

rearranges itself (B. **29**, R. 32). Cp. also the action of NaOH upon nitro-diamido-triphenyl-methane (C. 1897, II. 416); it is also obtained from formaldehyde, aniline, and phenyl-hydroxylamine (C. 1897, II. 1064); and, further, by heating p-diamido-diphenyl-methane with aniline and some oxidising agent (B. **25**, 302); by heating p-nitro-benzal chloride with aniline (B. **18**, 997); and by heating aurin to 120° with aqueous ammonia (B. **10**, 1016, 1123).

Nitrous acid converts it into aurin. Triphenyl-carbinol results when para-rosanilin diazo-chloride is decomposed with finely divided copper (B. **26**, 2225). At 180°–200° para-rosanilin is converted, by concentrated hydriodic acid, into aniline and p-toluidin. Evidence favouring the p-position of the two amido-groups is found in the conversion of p-rosanilin, by boiling hydrochloric acid, into p_2-diamido-benzo-phenone, which is also obtained from p-diamido-triphenyl-methane, the condensation product of benzaldehyde with aniline. Para-leucaniline, the reduction product from para-rosanilin, is also formed by the reduction of p_2-nitro-diamido-triphenyl-methane. The p-position of the three groups in the latter compound follows from the fact that it is produced by the same condensation reaction from p-nitro-benzaldehyde and aniline by which p-diamido-triphenyl-methane is made from benzaldehyde and aniline.

The rosanilin salts give a deeper blue shade than the salts of para-rosanilin (B. **15**, 680).

Homologous rosanilins have been prepared by the oxidation of a mixture of aniline and unsym. meta-xylidin (B. **15**, 1543), by condensation of p-nitro-benzaldehyde with o-toluidin, reduction and oxidation of the resulting condensation product (B. **15**, 679), and by the condensation of p-nitro-dimethyl-amido-benzo-hydrol with m-toluidin, etc. (B. **24**, 553).

Rosanilin-sulphonic acid, *acid fuchsine, fuchsine S*, is produced in the action of fuming sulphuric acid at 120° upon rosanilin. Nucleus-substituted fuchsines, see C. 1909, II. 362.

Alkylic Para-rosanilins.—The introduction of methyl residues into the amido-groups of rosanilin produces violet dyes—*methyl violet*. The violet colour assumes a deeper blue tint with the increase of methyl groups. These dyes are made by methylating para-rosanilin and by oxidising dimethyl-aniline. The methyl violets are reduced to leuco-compounds when they are heated with ammonium sulphide to 120°. Boiling hydrochloric acid resolves them into dimethyl-aniline and methylated p-diamido-benzo-phenones (B. **19**, 108).

Hexamethyl-para-rosanilin, *crystal violet* $[(CH_3)_2N.C_6H_4]_2.C{=}HC_6{=}N(CH_3)_2Cl$, is distinguished from the lower methyl derivatives by great power of crystallisation. It forms one of the principal constituents of methyl violet, and is produced (1) by the condensation of p_2-tetramethyl-diamido-benzo-phenone and dimethyl-aniline with dehydrating agents:

$$CO\begin{matrix}\diagup C_6H_4[4]N(CH_3)_2\\ \diagdown C_6H_4[4]N(CH_3)_2\end{matrix} + C_6H_5N(CH_3)_2HCl = C_{19}H_{22}N_2(CH_3)_6Cl + H_2O.$$

(2) By heating dimethyl-aniline with $COCl_2$ and $AlCl_3$ or $ZnCl_2$ (B. **18**, 767; R. **7**). Formic acid, formic ester, chloro-carbonic ester, perchloro-methyl-mercaptan, $CSCl_2$, etc., act the same as phosgene

(B. **19,** 109); (3) by oxidation of p_2-tetramethyl-diamido-diphenyl-methane with dimethyl-aniline; (4) by heating its methyl chloride or iodide to 110°–120°; (5) by oxidising its leuco-base.

p_3-Hexamethyl-triamido-triphenyl-carbinol, *crystal-violet base* $C(OH)[C_6H_4[4]N(CH_3)_2]_3$, melts at 195°. It is also formed by condensation of p-dimethyl-phenyl-magnesium bromide with p_2-tetramethyl-diamido-benzo-phenone (B. **36,** 4297). Tribromo-hydrate, see B. **33,** 753.

p_3-Hexamethyl-triamido-triphenyl-methane, *leuco-crystal violet* $CH[C_6H_4[4]N(CH_3)_2]_3$, melting at 173°, results by the reduction of *crystal violet*, by the condensation of ortho-formic ester and dimethyl-aniline with $ZnCl_2$, and by the condensation of p_2-tetramethyl-diamido-benzo-hydrol with dimethyl-aniline. Also by condensation of prussic sesqui-chlorohydrate with dimethyl-aniline, by way of tetramethyl-diamido-benzo-hydrylamine (C. 1900, I. 239).

Methyl violet is a mixture of hexamethyl-para-rosanilin with lower methylated derivatives (B. **19,** 107). It is produced in oxidising dimethyl-aniline, alone or when mixed with monomethyl-aniline, with iodine or chloranile, copper sulphate or chloride. When copper chloride is used it is advisable to add acetic acid or phenol.

Pentamethyl violet $C_{19}H_{12}N_3(CH_3)_5HCl$ is formed by oxidising **p_3-pentamethyl-triamido-triphenyl-methane** $[(CH_3)_2NC_6H_4]_2CH.C_6H_4[4]NH.CH_3$, melting at 116°. The latter can be isolated from the reduction-product of commercial methyl violet, a mixture of penta- and hexamethyl violet, by means of the acetyl derivative. This, when oxidised with acetyl-pentamethyl-rosanilin, yields a *green* dyestuff (B. **16,** 2906).

Tetramethyl violet is formed by oxidising **p_3-amido-tetramethyl-diamido-triphenyl-methane,** melting at 152°. The latter is a **tetramethyl-para-leucaniline** $NH_2[4]C_6H_4CH[C_6H_4[4]N(CH_3)_2]_2$, produced in the reduction of p-nitro-malachite green. Its acetyl derivative, like that of pentamethyl-leucaniline, yields a *green* dye upon oxidation.

Methyl green, *methyl chloride of hexamethyl-para-rosanilin chloride* $Cl(CH_3)_3N[4]C_6H_4C\begin{cases}C_6H_4[4]N(CH_3)_2\\ C_6H_4[4]N(CH_3)_2\end{cases}Cl$, is produced when methyl chloride acts upon an alcoholic solution of methyl violet heated to 40°, sodium hydrate being gradually added.

Alkylated Rosanilins.—When rosanilin is heated with methyl iodide, methyl chloride, ethyl iodide or chloride, and methyl or ethyl alcohol, three amide hydrogen atoms are replaced by methyl or ethyl radicles. The methyl base yields reddish-violet-coloured salts, and the ethyl base pure violet (Hofmann's *violet, dahlia*); these dissolve with difficulty in water, but dissolve easily in alcohol.

The violet dyes, by the addition of more methyl or ethyl groups, yield tetra-alkylic rosanilin iodides, which are capable of adding another molecule of methyl or ethyl iodide and forming **iodine greens** —*i.e. iodo-methylate of tetramethyl-rosanilin iodide* $C_{20}H_{16}(CH_3)_4N_3I.CH_3I+H_2O$, which has been displaced in the dye industry by methyl green (see B. **28,** 1008).

Aldehyde green (Usèbe, *J. pr. Ch.*, **92,** 337), another green rosanilin dye, has been prepared by heating rosanilin with aldehyde and sul-

phuric acid, and by further action of sodium hyposulphite. The most recent opinion is that in this reaction an aniline group has been changed to quinaldin, while the other two groups have occasioned the formation of aldol-aniline residues, which latter then add sulphur, just as is done by aldol-aniline itself (cp. B. **24,** 1700 ; **29,** 60).

Phenylated para-rosanilins.—Just as methyl violet is prepared from dimethyl-aniline by means of $COCl_2$, etc., so

Diphenylamine blue can be obtained by heating diphenylamine with carbon hexachloride C_2Cl_6 or oxalic acid to 120°. It is identical with **triphenyl-para-rosanilin** $C(OH)(C_6H_4.NH.C_6H_5)_3$ (B. **23,** 1964), obtained by the action of aniline upon para-rosanilin. By heating trianisyl-carbinol with aniline and benzoic acid we obtain the benzoate of the pure dye base; the latter is called **dianilino-fuchsone-anile** $(C_6H_5NH.C_6H_4)_2C : C_6H_4 : NC_6H_5$; it is a black crystalline powder, m.p. 238°, which on taking up water yields the colourless **p_3-trianilino-triphenyl-carbinol,** and, by reduction, **trianilino-triphenyl-methane** (B. **37,** 2870).

At present it is only the sodium salts of its mono- and disulpho-acids which are applied as *alkali blue* and *water blue* in dyeing.

Perchloro-formic ester $CClO_2CCl_3$, in a similar manner converts diphenyl-methylamine $(C_6H_5)_2N.CH_3$ into **trimethyl-triphenyl-para-rosanilin** $C(OH)\left(C_6H_4.N\langle\begin{matrix}CH_3\\C_6H_5\end{matrix}\right)_3$ (B. **19,** 278). Phosgene converts triphenylamine into the hydrochloride of **hexaphenyl-para-rosanilin** $C(OH)[C_6H_4.N(C_6H_5)_2]_3$ (B. **19,** 758). **Tricarbazol-carbinol** $C(OH)(C_{12}H_7NH)_3$ (B. **20,** 1904), is produced by heating together carbazol or diphenylimide and oxalic acid. It is analogous to the triphenyl-amine derivative.

Phenylated rosanilins are obtained by heating rosanilin hydrochloride with aniline or toluidins, or the free base with aniline and some benzoic acid. The **triphenyl-rosanilin hydrochloride** $C_{20}H_{16}(C_6H_5)_3N_3.HCl$ appeared in commerce as *aniline blue,* a bluish-brown crystalline powder, with copper lustre, soluble in alcohol but not in water. To dissolve it in the latter, sulpho-salts are prepared, which exhibit different shades of blue (*soluble blue*), corresponding to the number of sulpho-groups in them. At present diphenylamine blue, and other dyes, have taken its place. Diphenylamine results on distilling triphenyl-rosanilin.

By converting rosanilin, by means of the tridiazo-compound, into the *trihydrazin* derivative, there results **roshydrazin** $C(OH)(C_6H_5.NH.NH_2)_3$; this, by condensation with aldehydes and ketones, yields red and blue dyestuffs (B. **20,** 1557).

Other hexamethyl-triamino-triphenyl-carbinols have been obtained by transposition of the dimethyl-amido-benzoic esters with dimethyl-aniline-magnesium iodide $(CH_3)_2NC_6H_4MgI$ (A. **354,** 200).

3. *Phenol Derivatives of the Triphenyl-methanes.*—The phenol derivatives of the triphenyl-methanes are produced (1) from the corresponding amido-compounds through the diazo-derivatives ; (2) by condensations similar to those of the amido-compounds if phenols be substituted for the anilines ; (3) by the reduction of the phenol-carbinols into which they are changed by oxidation.

Monoxy-triphenyl-methanes.—**o-Oxy-triphenyl-methane** $(C_6H_5)_2CH.C_6H_4[2]OH$, m.p. 124°, from o-amido-triphenyl-methane (A. **241,** 367)

or the carbinol by reduction. **m-Oxy-triphenyl-methane**, m.p. 106° (A. **354**, 171). **p-Oxy-triphenyl-methane**, m.p. 110°, and **o-kresyl-diphenyl-methane** $(C_6H_5)_2CHC_6H_3[3]CH_3[4]OH$, m.p. 100°, from the carbinols or from benzo-hydrol with phenol and o-cresol respectively and $SnCl_4$ (B. **35**, 3137; **36**, 3561). By condensation of salicyl-aldehyde and anisaldehyde, with aniline sulphate, or dimethyl-aniline, and $ZnCl_2$, **oxy-diamido-triphenyl-methanes** have been obtained (B. **14**, 2522; **16**, 1307).

The **di-** and **trioxy-triphenyl-methanes** yield, on oxidation, di- and triphenol-carbinols, which, as a rule, possess the character of dye-substances. Carbinols in which two benzene nuclei are hydroxylated, and which correspond to the malachite-green compounds, are termed *benzeins*, and the corresponding dioxy-triphenyl-methanes, *leuco-benzeins*; whereas the derivatives with three hydroxylated benzene nuclei are called *aurins* or *rosolic acids*, while corresponding trioxy-triphenyl-methanes are designated as *leucaurins* or *leuco-rosalic* acids.

p_2-Dioxy-triphenyl-methane, *leuco-benzein*, *leuco-benzaurin* $C_6H_5.CH(C_6H_4[4]OH)_2$, m.p. 161°, is obtained (1) from p_2-diamido-triphenyl-methane (A. **206**, 153), (2) by reducing benzaurin (A. **217**, 230), as well as (3) by the condensation of benzaldehyde and phenol with sulphuric acid (B. **22**, 1944). It melts at 161°.

Dioxy-dimethyl-triphenyl-methane $C_6H_5CH[C_6H_3(OH)CH_3]_2$ melts at 170° (A. **257**, 70). **Phenyl-dithymol-methane** melts at 166°.

See B. **24**, R. 562, for the condensation of m-nitro-benzaldehyde with phenols.

p_3-Trioxy-triphenyl-methane, leucaurin [*triphenylol-methane*] $CH(C_6H_4[4]OH)_3$, is obtained in the reduction of aurin, its carbinol anhydride, by means of zinc dust and sodium hydrate or acetic acid. It crystallises in colourless needles, which become coloured on exposure to the air (A. **166**, 286; **194**, 136; **202**, 198). The *triacetate* melts at 138° (B. **11**, 1117).

p_3-Trianisyl-methane $(CH_3O[4]C_6H_4)_3CH$, m.p. 45°–47°, from anis-aldehyde and anisol with glacial acetic-sulphuric acid (B. **35**, 1197).

Leuco-rosolic acid $(HO[4]C_6H_4)_2.CH.C_6H_3[4]OH[3]CH_3$, results from the reduction of rosolic acid. Its *triacetate* melts at 148° (A. **179**, 198).

III. A. Phenol Derivatives of Triphenyl-carbinol.

These substances are formed by the oxidation of the oxy-triphenyl-methanes or their ethers. They may also be produced by the direct synthetic methods applicable to all triaryl-carbinols.

The p-hydroxylated triaryl-carbinols split off water more or less easily, turning into methylene-quinones or diaryl-quino-methanes. From p-oxy-triphenyl-carbinol we obtain, on heating, diphenyl-quino-methane, which may be regarded as the root-substance of the dye-stuffs of the triphenyl-methane series:

$$\underset{\text{p-Oxy-triphenyl-carbinol}}{(C_6H_5)_2C(OH)C_6H_4[4]OH} \xrightarrow{-H_2O} \underset{\text{Diphenyl-quino-methane, fuchsone.}}{(C_6H_5)_2C:C_6H_4:O}$$

A. *Triphenyl-carbinols hydroxylated in a Benzene Nucleus.*—**o-Oxy-triphenyl-carbinol**, m.p. 140°, from salicylic ester and phenyl-magnesium bromide. It turns into phenyl-xanthone on distillation in a vacuum.

m-Oxy-triphenyl-carbinol, m.p. 148° (A. **354**, 167). **p-Oxy-triphenyl-carbinol.** Two modifications, melting at 139° and 165° respectively, from p-oxy-triphenyl-acetic acid by expulsion of CO with H_2SO_4; also from the methyl ether, *p-anisyl-diphenyl-carbinol*, m.p. 84°, the condensation product of anisic acid ester with phenyl-magnesium-bromide. p-Oxy-triphenyl-carbinol, and p-methoxy-triphenyl-carbinol chloride, on heating to 200°, expel H_2O and CH_3Cl respectively, forming **diphenyl-quino-methane,** *fuchsone*, orange crystals, m.p. 168°, which easily takes up water and reverts into the carbinol. **Oxy-dibromo-triphenyl-carbinol; diphenyl-dibromo-quino-methane,** from **diphenyl-o-cresol-carbinol; diphenyl-methyl-quino-methane** (B. **36**, 3558). Diphenyl-quino-methanes are also produced by the condensation of diphenyl-ketene with excess of quinones, by splitting off CO_2 from the β-lactones first formed.

2, 5-Dioxy-triphenyl-carbinol, m.p. 136°, from gentisinic ester and C_6H_5MgBr. **2, 4-Dioxy-triphenyl-carbinol,** m.p. 124°, from benzo-resorcin and C_6H_5MgBr. **3, 4-Dioxy-triphenyl-carbinol,** by condensation of benzo-phenone chloride and pyro-catechin by means of concentrated H_2SO_4. On heating it expels water, and forms **3-oxy-fuchsone,** m.p. 123° (A. **372**, 82).

B. **Benzeïns** (see above) are produced by the condensation of benzo-trichloride with mono- and polyhydric phenols, in which the para-position with reference to a hydroxyl group is not substituted —*e.g.* o- and m-cresol, resorcinol, and pyro-catechin (but not p-cresol, hydroquinone, etc.) (B. **28**, R. 340). They are also formed when their leuco-compounds, the corresponding oxy-triphenyl-methanes, are oxidised.

The benzeïns are generally red-coloured compounds with metallic lustre. They dissolve on boiling with sodium bisulphite; acids precipitate them. Alkalies dissolve them with the formation of red or violet-coloured salts. The carbon dioxide of the air decomposes the latter.

p_2-Dioxy-triphenyl-carbinol, *phenol-benzeïn, benzaurin* $C_6H_5.C\langle{}^{C_6H_4.OH}_{C_6H_4.O}$ or $C_6H_5.C\langle{}^{C_6H_4.OH}_{C_6H_4=O}$, is produced in the condensation of benzo-trichloride and phenol (similar to the formation of malachite green) (A. **217**, 223), and by the oxidation of p-dioxy-triphenyl-methane, into which it passes upon reduction. It is a brick-red, crystalline powder. It breaks down, when fused with alkalies, into benzene and dioxy-benzo-phenone, and this latter decomposes further into para-oxy-benzoic acid and phenol. Its *diacetate* melts at 119°. Dimethyl ether, phenyl-p_2-dianisyl-carbinol, m.p. 77°, from phenyl-dianisyl-methane, the condensation product of benzaldehyde and anisol, yields, on boiling with dilute sulphuric acid, benzaurin (B. **36**, 2791).

p_2-Dioxy-m_2-dimethyl-triphenyl-carbinol, *o-cresol benzeïn* $C_6H_5.C(OH).[C_6H_3[3]CH_3[4]OH]_2$, melts at 220°–225° (A. **257**, 69). Further, dioxy-triphenyl-carbinols have been obtained from the corresponding dioxy-benzo-phenones with phenyl-magnesium bromide (A. **354**, 177).

The **oo'-dioxy-triphenyl-carbinols** are only known in the form of their anhydrides, the *phenyl-xanthydrols* $C_6H_5.C(OH)\langle{}^{C_6H_4}_{C_6H_4}\rangle O$. Special interest attaches to the phenyl-xanthydrols, hydroxylated or

amidated in the p-position, with regard to the central carbon atom, which split off water spontaneously and pass into the quinoid. *Phenyl-fluorones* $C_6H_5.C\begin{cases}[1]C_6H_4[6]\\ [1]C_6H_3\{[6]\\ [4]:O\end{cases}>O$ and phenyl-fluorimes $C_6H_5.C\begin{cases}C_6H_4\\ C_6H_3=NH\end{cases}>O$, the root-substances of the fluoresceïn and rhodamin dyes. The solutions of these compounds in alkalies or acids show a strong fluorescence.

Phenyl-fluorone $C_6H_5.C\begin{cases}C_6H_4\\ C_6H_3=O\end{cases}>O$, chrome-red needles, m.p. 207° is formed from the 4-amido-phenyl-fluorone by eliminating the amido-group, and by condensation of 4-methoxy-xanthone with C_6H_5MgBr and saponification of the methoxyl group with $AlCl_3$. It is insoluble in alkalies, but soluble in acids. By alcoholic potash the solution is made colourless, and the carbinol is formed (A. **372**, 293). **3-** and **5-Oxy-phenyl-xanthydrol,** m.p. 170° and 162° respectively, are similarly formed from 3- and 5-methoxy-xanthone.

Resorcin-benzeïn, *4-oxy-phenyl-fluorone* $C_6H_5.C\begin{cases}C_6H_3(OH)\\ C_6H_3(:O)—\end{cases}>O$, is formed when water acts upon the reaction product of resorcinol and benzo-trichloride (A. **217**, 234), and when $ZnCl_2$ acts upon benzoic acid and resorcin (*J. pr. Ch.* 2, **48**, 387). Also from 4-amido-phenyl-fluorone by way of the diazo-compound (A. **372**, 294). **Dinitro-resorcin-benzeïn,** see B. **26**, 2064.

vic-Resorcin-benzein, *2, 2'-dioxy-phenyl-xanthydrol* $C_6H_5.C(OH)\begin{cases}C_6H_3(OH)\\ C_6H_3(OH)\end{cases}>O$, from 2, 2'-dioxy-xanthone and C_6H_5MgBr (A. **372**, 132).

Hydroquinone-benzeïn, 3, 3'*-dioxy-phenyl-xanthydrol,* is obtained from 3, 3'-dimethoxy-xanthone and phenyl-magnesium bromide with subsequent saponification (A. **372**, 141), or by the condensation of benzaldehyde and hydroquinone by means of concentrated H_2SO_4 and oxidation of the resulting xanthene derivative with $FeCl_3$ (A. **372**, 301).

Oxy-hydroquinone-benzeïn, *phenyl-trioxy-fluorone* $C_6H_5C\begin{cases}C_6H_2(OH)_2\\ C_6H_2(OH):O\end{cases}>O$, by condensation of benzaldehyde and oxy-hydroquinone with sulphuric acid (B. **37**, 1171).

C. *Amido-oxy-triphenyl-carbinols.*—**4-Amido-phenyl-fluorone** $C_6H_5.C\begin{cases}C_6H_3(NH_2)\\ C_6H_3(:O)\end{cases}>O$, m.p. 305°, deep-red needles, obtained in the form of its acetyl compound by condensation of N-acetyl-m-amido-phenol with benzo-trichloride besides **4, 4'-diacetamido-phenyl-xanthydrol,** m.p. 248° (A. **372**, 322).

Rosamines.—These are the alkyl compounds of 4-amido-phenyl-fluorime. They are formed when monoalkylic and dialkylic o-amido-phenols act upon benzo-trichloride. While the benzeïns from phenols are very feeble dyes, whose alkali salts are even decomposed by carbon dioxide, the hydrochlorides of the rosamines are red and violet dyes, having great similarity to the rhodamines, possessing a blue tint and a redder fluorescence (B. **22**, 3001). They also result on heating resorcinol benzeïn with dimethyl- and diethyl-aniline.

The simplest, rosamine, **4-amido-phenyl-fluorime** $C_6H_5.C\begin{cases}C_6H_3(NH_2)——\\ C_6H_3(:NH_2Cl)\end{cases}>O$, is obtained in the form of its chlorohydrate

in red needles, from the 4, 4′-diacetamido-phenyl-xanthydrol by boiling with HCl (A. **372,** 316).

Rosamine chloride $C_6H_5C\langle^{C_6H_3}_{C_6H_3}\rangle$ $\begin{cases}[4]N(CH_3)_2\\[6]\end{cases}O$ $\begin{cases}[6]\\[4]=N(CH_3)_2Cl\end{cases}$ may be obtained from benzo-trichloride and dimethyl-amido-phenol. Red and blue mordant dyes are obtained by the condensation of proto-catechu-aldehyde with dialkyl-m-amido-phenols and with diakyl-anilines: *proto-red* (leuco-compound) $(HO)_2C_6H_3CH[C_6H_3(OH)N(CH_3)_2]_2$ and *proto-blue* (leuco-compound) $(HO_2)C_6H_3CH[C_6H_4N(CH_3)_2]_2$) (B. **36,** 2913).

D. **Aurins and Rosolic Acids.**—These compounds correspond perfectly to the rosanilins. The free p_3-trioxy-triphenyl-carbinols are not known. When freed from their salts they sustain an intramolecular anhydride formation.

These carbinol anhydrides are yellow in colour; their alkali salts dissolve in water, with a red colour. They are incompletely fixed by the fibre of the material, and are only applied in the form of lakes in the paper industry.

Aurin, para-rosolic acid, *yellow corallin* $\begin{matrix}HO[4]C_6H_4\\HO[4]C_6H_4\end{matrix}\rangle C\langle^{C_6H_4[4]}_{\quad\quad}\rangle O$, is produced (1) on boiling the diazo-hydrochloride of para-rosanilin with water (A. **194,** 301); (2) by the condensation of p-dioxy-benzo-phenone-chloride with phenol (B. **11,** 1350); (3) by the condensation of phenol with formic acid on heating with zinc chloride (*J. pr. Ch.*, 2, **23,** 549); and (4) by heating phenol (1 part) with oxalic acid ($\frac{2}{3}$ part) and sulphuric acid ($\frac{1}{2}$ part) to 130°–150° (A. **202,** 185). For the by-products arising when aurin is prepared by method 4, and for its separation from the same, see A. **194,** 123; **196,** 77; B. **28,** R. 743.

Aurin dissolves in glacial acetic acid and alcohol with a yellowish-red colour, crystallises in dark-red needles or prisms with metallic lustre, and decomposes when heated above 220°. It dissolves in alkalies with a fuchsine-red colour. With the primary alkaline sulphites it readily yields colourless, crystalline derivatives, decomposable by acids and alkalies. Aurin forms crystalline compounds with hydrochloric acid. Water decomposes them. Digested with zinc dust and hydrochloric acid or acetic acid, aurin is reduced to leucaurin or p_3-trioxy-triphenyl-methane. Heated to 250° with water, it breaks up into p_2-dioxy-benzo-phenone and phenol.

Aurin is changed to para-rosanilin when it is heated with aqueous ammonia to 150°. An intermediate product (having 1 or 2 amide groups) is the so-called *peonine* (red corallin). With aniline we obtain triphenyl-para-rosanilin, and the intermediate product is *azulin*. Consult B. **29,** R. 510, for isomeric *acetyl-aurins*. **Dimethyl-aurin**, m.p. 183°–186°, is easily formed by methylation of aurin with diazo-methane in ether suspension (M. **29,** 653).

p_3-Trianisyl-carbinol $(CH_3O[4]C_6H_4)_3COH$, m.p. 84°, colourless crystals, from p_3-trianisyl-methane with PbO_2; its OH group is more capable of reaction than that of triphenyl-carbinol. It even transposes to trianisyl-aceto-nitrile with prussic acid. o_3-, m_3-, and o_2p-Trianisyl carbinols, m.p. 181°, 119°, and 110° respectively, have been prepared

from the magnesium compounds of o- and m-iodanisol with o-, m-, and p-methoxy-benzoic ester (B. **35,** 3024).

Rosolic acid $C_{20}H_{16}O_3$ is the inner anhydride of *p_3-trioxy-diphenyl-m-tolyl-carbinol.* Rosolic acid, like aurin, is obtained by boiling the diazo-chloride of rosanilin with water (A. **179,** 192) and by oxidising a mixture of phenol and cresol $C_6H_4(CH_3)OH$ with arsenic acid and sulphuric acid, whereby the linking menthane carbon is furnished by the methyl group. When rosolic acid is digested with alcohol and zinc dust, it is reduced to leuco-rosolic acid, from which it is obtained by oxidation (B. **26,** 254).

Trioxy-aurin $C_{19}H_{14}O_6$ results from the interaction of $ZnCl_2$, pyrocatechin, and formic acid (B. **26,** 255). **Resaurin** $C_{19}H_{14}O_6$ is similarly prepared with resorcin (*J. pr. Ch.* 2, **28,** 547). **Orcin-aurin** $C_{22}H_{18}O_6$ (*J. pr. Ch.* 2, **25,** 277; B. **18,** 546). **o-Amino-aurin,** see B. **40,** 3588.

Eupittonic acid, *eupitton, hexamethoxy-aurin* $C_{19}H_8(OCH_3)_6O_3$, is produced by oxidising a mixture of the dimethyl ester of pyrogallic acid and methyl-pyrogallic acid. It is, therefore, an aurin in which six methoxyl groups are present. It forms orange-yellow crystals, melting with decomposition at 200°. It dissolves with a deep blue colour in alkalies, yielding salts which are precipitated by excess of alkali (B. **12,** 2216). Reichenbach (1835) observed the formation of a blue-coloured barium salt when fractions of beechwood-tar were allowed to stand with baryta water, and named it *pittical* (from πίττα, tar, and κάλλος, beauty). When heated with ammonia, eupittonic acid, just like aurin, affords an *hexamethoxyl-rosanilin. Tetra-* and *hexamethoxy-triphenyl-carbinol,* see B. **41,** 4423.

Alcohols and Aldehydes of Triphenyl-methane.—Few of them are known: **phenol-phthalol** $(HOC_6H_4)_2CHC_6H_4[2]CH_2OH$, melting at 190°, was prepared by the action of sodium amalgam upon phenol-phthaleïn (A. **202,** 87).

p-Diphenyl-methyl-benzaldehyde $(C_6H_5)_2CH[4]C_6H_4.CHO$, boiling at 190°–195° (46 mm.), results from the condensation of terephthal-aldehyde and benzene with concentrated sulphuric acid (B. **19,** 2029). *Dialdehydes* have been prepared by the condensation of benzaldehyde, m- and p-nitro-benzaldehyde with vanillin by means of $ZnCl_2$.

Benzal-divanillin $C_6H_5CH[C_6H_2(OH)(OCH_3)CHO]_2$, m.p. 222°; **m-** and **p-nitro-benzal-divanillin,** m.p. 266° and 276° with decomposition (B. **36,** 3975).

Carboxyl Derivatives of Triphenyl-methane.— Triphenyl-methane-carboxylic acids are produced (1) by reduction of triphenyl-carbinol-carboxylic acids; and (2) from their nitriles. The latter are prepared by the action of aluminium chloride upon the cyano-benzal chlorides and benzene.

Triphenyl-methane-o-carboxylic acid, *benzol phthalin* (see Phthaleïns), $(C_6H_5)_2CH.C_6H_4[2]CO_2H$, m.p. 162°, is isomeric with triphenyl-acetic acid, and is produced by the reduction of diphenyl-phthalide (2), the lactone of triphenyl-carbinol-o-carboxylic acid (A. **202,** 52), and its nitrile. Chromic acid oxidises it to diphenyl-phthalide, while it breaks down into carbon dioxide and triphenyl-methane when it is heated with barium hydroxide. Sulphuric acid rearranges it to phenyl-anthranol $C_6H_5CH\langle{}^{C_6H_4}_{C_6H_4}\rangle CO$.

o-Cyano-triphenyl-methane $(C_6H_5)_2CH.C_6H_4[2]CN$ melts at 89° and boils at 270°–285° (70–85 mm.). Preparation, see above (B. **24,** 2572).

p_2-Tetramethyl-diamido-triphenyl-methane-o-carboxylic acid $[(CH_3)_2N[4]C_6H_4]_2.CH.C_6H_4[2]CO_2H$, from tetramethyl-diamido-diphenyl-phthalide (A. **206,** 101), melts at 200°.

Triphenyl-methane-p-carboxylic acid melts at 161°, and its *nitrile* at 91° (B. **26,** 3079). **Methyl-triphenyl-methane-carboxylic acids,** see B. **16,** 2364; **19,** 3064; A. **234,** 242.

Oxy-triphenyl-methane-carboxylic acids are formed in the reduction of the oxy-triphenyl-carbinol-carboxylic acids. **p-Oxy-triphenyl-methane-o-carboxylic acid** $\begin{matrix} HO[4]C_6H_4 \\ C_6H_5 \end{matrix}\!\!>\!CH.C_6H_4[2]CO_2H$, melting at 210° (B. **18,** 1616), and **p_2-dioxy-triphenyl-methane-o-carboxylic acid,** *phthalin* $[HO[4]C_6H_4]_2CH.C_6H_4[2]CO_2H$, melting at 225° (A. **202,** 36, 153), were obtained from the corresponding oxy-triphenyl-carbinol-o-carboxylic acids. Concentrated sulphuric acid converts them into the corresponding oxy-phenyl-anthranols.

Hydrofluoranic acid $C_6H_4\begin{cases}[1]CH\begin{matrix}C_6H_4[2] \\ C_6H_4[2]\end{matrix}\!\!>\!O \\ [2]CO_2H\end{cases}$, melting at 226°–228°, results from the reduction of fluorane and tribromo-fluorane. When the acid is distilled over lime, *xanthone* and benzene result, while diphenylene-phenyl-methane (B. **25,** 3586) is produced in its distillation over baryta or soda-lime.

Fluorescine, p_2-dioxy-hydrofluorane-carboxylic acid, is the reduction product of fluoresceïn.

p_2-Dioxy-triphenyl-methane-m_2-dicarboxylic acid is formed by condensation of benzaldehyde with salicylic acid by means of gaseous HCl (C. 1909, I. 747).

Carboxyl Derivatives of Triphenyl-carbinol, Phthalides.—The o-carboxyl derivatives of this class are especially noteworthy. They cannot exist free; they lose water and form lactones, which can be regarded as diphenylated phthalides.

Diphenyl-phthalide, *triphenyl-carbinol-o-carboxylic acid lactone* $C_6H_4\begin{cases}[1]C=(C_6H_5)_2 \\ [2]COO\end{cases}$, melting at 115°, is formed (1) by the oxidation of triphenyl-methane-o-carboxylic acid, (2) in slight amount by the action of mercury diphenyl upon phthalyl chloride, (3) from phthalyl chloride and benzene with aluminium chloride. The third method of formation serves for the preparation of diphenyl-phthalide, formerly considered to be o-phthalo-phenone, until it was discovered to contain a lactone, the basis of the phthaleïns.

In the third method of producing diphenyl-phthalide the phthalyl chloride may be replaced by phthalic anhydride. In this case o-benzoyl-benzoic acid will be the first product, which by the further action of benzene and aluminium chloride changes to diphenyl-phthalide. The acetyl derivative of o-benzoyl-benzoic acid is better adapted for the formation of diphenyl-phthalide than the free acid (B. **14,** 1865).

Diphenyl-phthalide, when boiled with alkalies, forms salts of triphenyl-carbinol-o-carboxylic acid, from the solution of which acids re-precipitate diphenyl-phthalide. Zinc dust in alkaline solution

reduces triphenyl-carbinol-o-carboxylic acid to triphenyl-methane-o-carboxylic acid.

The **anilide** $C_6H_4\{^{[1]C=(C_6H_5)_2}_{[2]CO.NH.C_6H_5}$, m.p. 189°, and the **hydrazide** $C_6H_4\{^{[1]C=(C_6H_5)_2}_{[2]CON_2HC_6H_5}$, m.p. 230°, are produced on boiling diphenyl-phthalide and aniline hydrochloride (B. **27,** 2793) with phenyl-hydrazin (B. **26,** 1273).

Dithio-diphenyl-phthalide $C_6H_4\{^{[1]C=(C_6H_5)_2}_{[2]CSS}$, from diphenyl-phthalide with sulphuretted phosphorus, see C. 1900, II. 575.

The nitration of diphenyl-phthalide produces two *dinitro-diphenyl-phthalides*, from which two *diamido-diphenyl-phthalides* have been obtained (A. **202,** 66).

p₂-Tetramethyl-diamido-diphenyl-phthalide $C_6H_4\{^{[1]C=[C_6H_4[4]N(CH_3)_2]_2}_{[2]COO}$ m.p. 190°, is obtained in the condensation of phthalic anhydride and dimethyl-aniline with $ZnCl_2$. If phthalic anhydride be substituted for phthalyl chloride in this reaction there is an isomeric body, *phthalyl green*, produced. This is probably an anthracene derivative, which is also related to malachite green, and owes its origin to an admixture of the phthalyl chloride to the phthalylene tetrachloride (C. 1898, I. 330; 1903, I. 85). The esters of the colourless tetramethyl-diamido-diphenyl-phthalide form intensely blue quinoid dyeing salts with acids.

Triphenyl-carbinol-m-carboxylic acid, m.p. 161°, and **triphenyl-carbinol-p-carboxylic acid,** m.p. 200°, are formed when diphenyl-m-tolyl-methane and diphenyl-p-tolyl-methane are oxidised with chromic acid in glacial acetic acid solution. The latter also appears in the oxidation of p-diphenyl-methyl-benzaldehyde, and of triphenyl-methane-p-carboxylic acid (B. **16,** 2369; **26,** 3081; **37,** 657).

Phenyl-p-tolyl-phthalide is made from acetyl-o-benzoyl-benzoic acid, toluol, benzoyl-o-benzoic acid chloride and toluol, toluic-o-benzoic acid chloride, and benzene with aluminium chloride (B. **14,** 1867; **29,** R. 995). *Isomeric methylated diphenyl-phthalides* are produced in the oxidation of diphenyl-m- and p-xylyl-methanes. **Ditolyl-phthalide** melts at 116° (C. 1898, I. 209; A. **299,** 286). See B. **28,** 513, for **di-biphenyl-o-phthalide** $C_6H_4\{^{[1]CO.O}_{[2]C=(C_6H_4.C_6H_5)_2}$.

Carboxyl Derivatives of the Oxy-triphenyl-carbinols.—The *phthaleïns*, the derivatives of phthalide containing two phenol residues, are particularly important, and are dyes which are of great technical value. A. v. Baeyer discovered them in 1871. The transition from them to diphenyl-phthalide is found in—

Benzol-phenol-phthalide $C_6H_4\{^{[1]C<^{C_6H_4OH}_{C_6H_5}}_{[2]COO}$, m.p. 167°. It is prepared from o-benzoyl-benzoic acid, phenol, and sulphuric acid (A. **354,** 171). Similarly we obtain: **Resorcyl-phenyl-phthalide,** m.p. 109°; **pyro-catechin-phenyl-phthalide,** m.p. 161°; **hydroquinone-phenyl-phthalide,** m.p. 247°; **pyrogallol-phenyl-phthalide,** m.p. 189° (A. **372,**

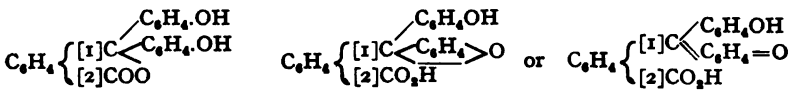
91). Of the polyoxy-diphenyl-phthalides mentioned, the p-substituted ones dissolve in alkalies with a *red* colour, splitting the lactone ring and forming p-quinoid salts (cp. Phenol-phthaleïns).

The **phthaleïns** result from the condensation of phthalic anhydride (1 mol.) with phenols (2 mols.) on heating with sulphuric acid, or, better, with $SnCl_2$ to 120° (or with oxalic acid at 115°).

The phthaleïns derived from di- and polyhydric phenols are all anhydrides, formed by the elimination of water from two phenol-hydroxyls (A. **212**, 347), in union with different benzene nuclei. In the condensation of phthalic anhydride and phenol-p_2-dioxy-diphenyl, phthalide, or phenol-phthaleïn, is not the only product; *fluorane*, the anhydride of o_2-dioxy-diphenyl-phthalide, is also formed. It is the simplest representative of the phthaleïn anhydrides, which contain a ring similar to the xanthone ring.

The free phthaleïns are generally colourless, crystalline bodies. They dissolve in the alkalies with intense colorations, and are again separated from their solutions by acids (even CO_2). The addition of concentrated caustic alkali causes the colours to disappear. On diluting with water, the colours reappear.

To show the similarity of the phthaleïns to the aurins or rosanilins in the formula, it is assumed that the free, colourless phthaleïns contain the lactone ring; in their coloured alkali salt solutions this ring is absent, and the methane carbon atom and an oxygen atom form a quinone-like union with a benzene nucleus. This idea is apparently supported by the preparation of phthaleïn-oxime:

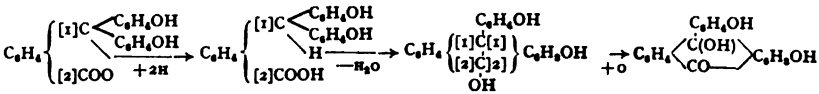


Free phenol-phthaleïn — Phenol-phthaleïn in coloured alkali salts.

This view is supported by the fact that the mm'-dioxy-ditolyl-phthalide, which, on account of the non-existence of m-quinones, cannot be analogously formulated, is dissolved quite colourlessly in alkalies. Much excess of alkali decolourises the solutions of phenol-phthaleïn with formation of salts of the carbinol $NaO_2CC_6H_4.C(OH)(C_6H_4ONa)_2$ (C. 1904, I. 1088).

It should be added that lactone esters and ethers have also been obtained by acidulation and alkylisation of phenol-phthaleïn in alkaline solution (B. **28**, 3258; **29**, 131; cp. B. **29**, R. 552).

The phenol-phthaleïns, by reduction, yield oxy-triphenyl-methane-carboxylic acids—the *phthalins*. The latter are changed by concentrated sulphuric acid into oxy-phenyl-anthrone derivatives, called *phthalidins*. The oxidation of the latter produces the *phthalideïns*, or oxy-phenyl-oxanthrone derivatives. The following diagram represents these changes, with phenol-phthaleïn as the example:



Phthaleïn, p_2-dioxy-diphenyl-phthalide — Phthalin, p_2-dioxy-triphenyl-methane-o-carboxylic acid — Phthalidin, dioxy-phenyl-anthrone — Phthalideïn, dioxy-phenyl-oxanthrone.

Phenol-phthaleïn, *p_2-phthaleïn, dioxy-diphenyl-phthalide* $C_{20}H_{14}O_4$, is a yellow powder, crystallising from alcohol in colourless crusts, and melting at 250°. It dissolves in the alkalies with a red colour. It is used as an indicator in alkalimetry, especially in determining carbon dioxide with baryta (B. **17,** 1907). It is formed from phthalo-phenone when nitrous acid acts on the p-diamido-compound; by oxidising an alkaline solution of the corresponding phthalin with air, or with potassium ferricyanide or potassium permanganate, and is also obtained on heating phthalic anhydride with phenol and tin chloride, or with sulphuric acid to 115°–120° for eight hours. o_2-Dioxy-diphenyl-phthalide anhydride, insoluble in caustic potash, is a by-product, sometimes also fluorane (A. **202,** 68). Boiling caustic potash and zinc dust reduce phthaleïn to phthalin, and it is decomposed into p_2-dioxy-benzo-phenone and benzoic acid by fusion with caustic potash.

Derivatives of Phenol-phthaleïn.—**Diaceto-phenol-phthaleïn** melts at 143°. **Dibenzoyl-phenol-phthaleïn** melts at 169° (B. **29,** 131).

Phenol-phthaleïn methyl ester $CH_3OCOC_6H_4.C\langle^{C_6H_4:O}_{C_6H_4.OH}$, m.p. 127°–130°, orange needles, is formed by esterification of phenol-phthaleïn with methyl-alcoholic H_2SO_4; it dissolves in alkalies with a violet colour, and is easily re-saponified to phenol-phthaleïn (B. **40,** 3484, 3726). The lactoid **phenol-phthaleïn mono-** and **dimethyl** ethers, m.p. 149° and 100°, are obtained by alkylation of phenol-phthaleïn in alkaline solution (B. **40,** 3729). The latter has also been obtained synthetically from phthalic anhydride, anisol, and $AlCl_3$ (B. **29,** R. 550).

Phenol-phthaleïn-anilide $C_6H_4\begin{cases}[1]C=(C_6H_4.OH)_2\\ \diagdown\\ [2]CONC_6H_5\end{cases}$, m.p. 279° (B. **26,** 3077).

Phenol-phthaleïn-oxime $(C_{20}H_{14}O_3):NOH$ (?), a yellow crystalline powder, melting with decomposition at 221°, and produced by the action of hydroxylamine upon an alkaline phenol-phthaleïn solution. With dimethyl sulphate in alkaline solution it gives a dimethyl ether. This indicates a formula of the lactame type $C_6H_4\begin{cases}C(C_6H_4.OH)_2\\ CO\end{cases}\rangle NOH$. Boiling dilute sulphuric acid decomposes the oxime into p-oxy-o-benzoyl-benzoic acid and p-amido-phenol (B. **42,** 2825). **Tetrachloro-phenol-phthaleïn** $C_{20}H_{10}Cl_4O_4$, m.p. above 300° (C. 1909, II. 127). **Tetrabromo-phenol-phthaleïn,** m.p. 220°–230° with decomposition. **Tetra-iodo-phenol-phthaleïn** is used commercially as an iodoform substitute under the name "*nosophene.*"

Tetrabromo-phenol-phthaleïn-oxime (B. **26,** 2260; C. 1900, I. 1291). Quinoid **tetrabromo-phenol-phthaleïn-mono-** and **-diethyl ether,** see B. **40,** 1437.

m, m-Dioxy-p-ditolyl-phthalide, m.p. 206°, see A. **354,** 185.

Fluorane, *o_2-phenol-phthaleïn anhydride* $C_6H_4\begin{cases}[1]C\langle^{C_6H_4[2]}_{C_6H_4[2]}\rangle O,\\ [2]COO\end{cases}$ melting at 173°–175°, is produced, together with p_2-phenol-phthaleïn, by the condensation of phthalic anhydride and phenol. Fluorane yields hydro-fluoranic acid by reduction, and diphenylene-phenyl-methane when it is distilled over zinc dust (B. **25,** 3586). The *anile* $C_6H_4\begin{cases}[1]C=(C_6H_4)_2O\\ \diagdown\\ [2]CON.C_6H_5\end{cases}$ melts at 242° (B. **27,** 2793). **Tribromo-fluorane**

$C_{20}H_{10}.Br_2O_3$, m.p. 298°–300°, is produced by the action of PBr_5 upon fluoresceïn, and is reduced by alcoholic caustic soda and zinc dust to hydro-fluoranic acid (B. **25,** 1388). Concerning **nitro-fluoranes,** see B. **31,** 1739; **32,** 1131, 2108. **3, 6-Dimethyl-fluorane,** m.p. 213°, see C. 1910, I. 449.

The **fluoresceïns** are the o-phthalic anhydrides produced by the condensation of phthalic anhydrides with resorcin. They are characterised by a beautiful fluorescence; this is especially true of their alkaline solutions (Baeyer, A. **183,** 1).

Phthalic anhydride may also be replaced by the anhydrides of aliphatic dicarboxylic acids. When succinic, maleic, and citraconic anhydrides are condensed with resorcin, the corresponding fluoresceïns are produced. Pyro-mellithic and mellithic acids, and their anhydrides, also combine with resorcin to form dyestuffs resembling fluoresceïn, and these contain 1, 2, or 3-fold xanthyl groups (C. 1907, I. 549).

See also o-sulpho-benzoic acid and naphthalic acid (B. **15,** 883; **18,** 2864; **24,** R. 763; **26,** R. 542; **29,** 2824). **Hydroquinone-succineïn,** C. 1908, II. 786; **pyrogallol-succineïn,** C. 1899, II. 758.

Resorcin-phthaleïn, fluoresceïn $C_{20}H_{12}O_5$, is prepared by heating phthalic anhydride (2 parts) with resorcin (7 parts) to 200°, or with anhydrous oxalic acid (B. **17,** 1079) to 110°–117°. When precipitated from its salts it occurs in yellowish-red flakes $C_{20}H_{14}O_6$, which quickly lose water, and become $C_{20}H_{12}O_5$, which dissolves in alcohol with a yellow-red colour and green fluorescence, and dries out as a red powder. Upon reduction fluoresceïn yields fluorescin, and PCl_5 converts it into *fluoresceïn chloride, p_2-dichloro-fluorane* (see Rhodamines). On treatment with alcoholic KSH this yields thio-fluoresceïn $C_6H_4O_2 : (C_6H_3.SH)_2 : O$ (B. **32,** 1127).

Baeyer ascribed the formula $C_6H_4\begin{cases}[1]C=(C_6H_3OH)_2O \\ [2]COO\end{cases}$ to fluoresceïn.

As there was a disposition to assume that the phthalic acid residue replaced both m-hydrogen atoms (5) in the resorcin molecules, R. Meyer showed that fluoresceïn is a dioxy-derivative of o-phenol-phthaleïn anhydride, for which reason he gave it the name *fluorane* (above); and that, therefore, the phthalic acid residue occupied the o-position with reference, at least, to each of the hydroxyl group of the resorcin molecule, and between these hydroxyl groups the anhydride formation occurred. R. Meyer converted fluoresceïn (1) by means of PBr_5 into tribromo-fluorane (2), which, like fluorane (4) itself, yields hydro-fluoranic acid (3) upon reduction. Fluoresceïn and fluorane contain a ring, closely related to the xanthone ring; indeed, hydro-fluoranic acid may be decomposed into xanthone and benzene:

$$\overset{(1)}{C_6H_4}\begin{cases}[1]C<\begin{matrix}C_6H_3(OH)[6]\\C_6H_3(OH)[6]\end{matrix}\\[2]COO\end{cases}O \longrightarrow \overset{(2)}{C_{20}H_9Br_3O_3} \longrightarrow \overset{(3)}{C_6H_4}\begin{cases}[1]CH<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}O\\[2]COOH\end{cases} \longleftarrow \overset{(4)}{C_6H_4}\begin{cases}[1]C<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}O.\\[2]COO\end{cases}$$

The intense colour of fluoresceïn led Bernthsen and others to ascribe a quinoid constitution to free fluoresceïn and its coloured derivatives (see Phenol-phthaleïn). The assumption of a free carboxyl group in fluoresceïn is supported by its solubility in sodium bicarbonate, and its esterification with alcohol and sulphuric acid (see below).

The colourless derivatives were supposed to have their origin in the lactone formula of fluoresceïn. This view allies fluoresceïn and its coloured derivatives with the aurins and rosanilins.

When fluoresceïn is fused with caustic soda it breaks down into resorcinol and monoresorcinol-phthaleïn, or dioxy-benzoyl-benzoic acid. Bromine in glacial acetic acid changes the latter to dibromo-dioxy-benzoyl-benzoic acid, which fuming sulphuric acid rearranges to dibromo-xantho-purpurin; it is also obtained from eosin. Hence it follows that monoresorcinol-phthaleïn is 2, 4-dioxy-o-benzoyl-benzoic acid, because if it were 2, 6-dioxy-o-benzoyl-benzoic acid it would be impossible for an anthraquinone condensation to occur (Heller, B. **28,** 314; B. **29,** 2623).

Derivatives of Fluoresceïn.—**Fluoresceïn-anilide** and **fluoresceïn-phenyl-hydrazide** $C_6H_4\begin{cases}C(C_{12}H_8O_3)\\ CONC_6H_5\end{cases}$ and $C_6H_4\begin{cases}C(C_{12}H_8O_3)\\ CON_2HC_6H_5\end{cases}$, from fluoresceïn on heating with aniline or phenyl-hydrazin, form colourless crystals; the anilide yields a dimethyl ether, m.p. 207° (B. **28,** 396; **32,** 1133).

Fluoresceïn-carboxyl-methyl ester $CH_3OCO[2]C_6H_4C\begin{cases}C_6H_3(OH)\\ O\\ C_6H_3{=}O\end{cases}$, m.p. 252°, iridescent green crystals, is formed by the esterification of fluoresceïn with sulphuric acid and methyl alcohol (B. **34,** 2641). On further methylation with dimethyl sulphate in nitro-benzol solution it yields the **quinoid fluoresceïn-dimethyl-ether ester** $CH_3OCOC_6H_4C\begin{cases}C_6H_3(OCH_3)\\ >O\\ C_6H_3{=}O\end{cases}$, m.p. 177°, brick-red needles (B. **28,** 396), besides the colourless **lactoid dimethyl ether** $C_6H_4\begin{cases}C<\begin{matrix}C_6H_3(OCH_3)\\ C_6H_3(OCH_3)\end{matrix}>O\\ COO\end{cases}$, m.p. 198°, probably produced by isomerisation (cp. B. **40,** 3603). The latter is also obtained from its anilide upon heating with concentrated sulphuric acid. The latter, on esterification with methyl alcohol and HCl, passes into the trimethyl ether of dioxy-xanthydrol-carboxylic acid, which possesses strong basic properties and forms, with acids, highly coloured salts soluble in water without hydrolysis (A. **371,** 326), corresponding to the coloured salts of triphenyl-carbinol (cp. A. **370,** 142).

Substituted Fluoresceïns.—Although fluoresceïn itself is not applicable as a dye, by introducing halogens and nitro-groups into it dyestuffs of remarkable beauty can be obtained. If we start with fluoresceïn, then the substitution will occur in the resorcinol residues.

If bromine be allowed to act on fluoresceïn suspended in glacial acetic acid, **eosin, tetrabromo-fluoresceïn** $C_{20}H_8Br_4O_5$ is produced. Crystallised from alcohol it forms red crystals. The *potassium* and *sodium salts* constitute the eosin of commerce, soluble in water, and imparting to wool and silk a beautiful rose-colour. In the case of the sodium salt there is a yellowish-red fluorescence (Caro, 1873).

Erythrosin, *tetra-iodo-fluoresceïn* $C_{20}H_8I_4O_5$.

Safrosine, *eosin scarlet,* dibromo-dinitro-fluoresceïn $C_{20}H_8Br_2(NO_2)_2O_5$, is formed when bromine acts upon dinitro-fluoresceïn, or when nitric acid acts upon di- or tetra-bromo-fluoresceïn (A. **202,** 68). See B. **30,**

333, for the dinitro-fluoresceïn yellow from dinitro-fluoresceïn and ammonia.

To obtain the fluoresceïns substituted in the phthalic acid residue, condense the chlorinated phthalic anhydrides with resorcinol (Noelting). The bromo- and iodo-fluoresceïns, with the substituents in the resorcinol residues, are at the same time prepared from the chlorinated bodies :

Phloxin, *tetrabromo-dichloro-* and *tetrabromo-tetrachloro-fluoresceïn* $C_{20}H_4Cl_4Br_4O_5$, **rose Bengal,** *tetra-iodo-tetrachloro-fluoresceïn.*

Phthalic anhydride has also been condensed with pyro-catechol (B. **40,** 1442), *hydroquinones, orcins,* and *phloro-glucin.*

Hydroquinone-phthaleïn, m.p. 226°, is formed from hydroquinone and phthalic anhydride, as well as from fluorane, by transforming into 2, 7-dinitro-fluorane, diamido-fluorane, and treating the latter with nitrous acid (B. **28,** 2959 ; **31,** 1743). It shows no fluorescence, and it also differs from fluoresceïn in colour ; it approaches phenol-phthaleïn in its behaviour (B. **36,** 2949). In alkalies, hydroquinone-phthaleïn dissolves with a violet and somewhat unstable colour, o-quinoid salts being produced with a probable splitting of the xanthone ring (cp. hydroquinone-benzeïn, above, and A. **372,** 133). For esters of hydroquinone-phthaleïn, see A. **372,** 298. The condensation of phthalic anhydride with orcin produces three **orcin-phthaleïns ;** only that orcin-phthaleïn which contains two hydroxyl groups in the p-position, *i.e.* the phthalic residue, turns out to be a perfect analogue of fluoresceïn (B. **29,** 2630).

Pyrogallol-phthaleïn, gallein $HOCO[2]C_6H_4C\begin{matrix}/C_6H_2(OH)_2\backslash O\\ \backslash C_6H_2(OH)/O\end{matrix}$ (?) is obtained on heating pyrogallic acid with phthalic anhydride to 200°. It forms crystals with green colour, dissolving with a dark-red colour in alcohol and with a beautiful blue colour in excess of alkalies.

It is converted by concentrated sulphuric acid into *cœruleïn* (see A. **209,** 249). The latter is a permanent green anthracene dyestuff (A. **209,** 249 ; C. 1900, II. 100 ; 1901, II. 775). **Tetrachloro-gallein,** see C. 1909, II. 2161.

Oxy-hydroquinone-phthaleïn, like the isomeric galleïn, and in contrast with **phloro-glucin-phthaleïn,** which does not contain the hydroxyl groups in the ortho-position, is an excellent mordant for cotton. Like galleïn, it is condensed by concentrated sulphuric acid to an anthracene derivative violeïn ; oxy-hydroquinone reacts like resorcin with many other 1, 2-dicarboxylic anhydrides, with formation of phthaleïn (B. **34,** 2617, 2637 ; **35,** 1782 ; **36,** 1070).

The **rhodamins,** the phthaleïns of m-amido-phenol and its derivatives, are of special importance. They are violet-red, magnificently fluorescent dyestuffs. In constitution they are perfectly analogous to the fluoresceïns.

The *simplest* rhodamin is formed when m-amido-phenol hydrochloride and phthalic anhydride are heated to 190° with concentrated sulphuric acid (B. **21,** R. 682).

The *alkylic rhodamins* possess more intense colours. They are produced when rhodamin hydrochloride is heated with alkyl iodides. A better course to pursue is the condensation of alkylic m-amido-phenols and phenyl-m-amido-phenol with phthalic anhydride (B. **21,**

R. 682, 920; **22,** R. 788). Still another procedure consists in rearranging fluorescein chloride, melting at 252° (the product of the action of PCl_5 upon fluorescein), by heating it with dialkylamines (B. **22,** R. 625, 789).

Anisolines, alkyl ethers of the rhodamins (?)—see B. **25,** R. 866.

Succino-rhodamin has been obtained from succinic anhydride and m-amido-phenol (B. **28,** R. 532).

Di-salicylic acid phthalide $C_6H_4\begin{cases}[1]C[C_6H_3(OH)COOH]_2\\ [2]COO\end{cases}$, m.p. 276° with decomposition, is formed besides phthaloyl-salicylic acid from phthalic anhydride, salicylic ester, and $AlCl_3$ (A. **303,** 280).

III. B. **p-Phenylene-bis-diphenyl-methane** $C_6H_4\langle^{CH(C_6H_5)_2}_{CH(C_6H_5)_2}$, from the corresponding glycol by reduction with zinc and glacial acetic acid. Derivatives of this hydrocarbon are obtained by the introduction of the $CH(C_6H_5)_2$ group into quinones and quinoid substances by means of benzo-hydrols.

Benzo-quinone-bis-diphenyl-methane $C_6H_2O_2[CH(C_6H_5)_2]_2$, m.p. 250°. **Benzo-quinone-bis-tetramethyl-diamido-diphenyl-methane,** m.p. 245°, from tetramethyl-diamido-benzo-hydrol and quinone on heating in alcoholic solution (B. **32,** 2146).

p-Phenylene-bis-diphenyl-carbinol, *tetraphenyl-p-xylylene-glycol* $(C_6H_5)_2C(OH)[1]C_6H_4[4]C(OH)(C_6H_5)_2$, m.p. 169°, is obtained from terephthalic ester and C_6H_5MgBr. On boiling with silver, the benzene solution of the bromide $(C_6H_5)_2CBrC_6H_4CBr(C_6H_5)_2$ gives **tetraphenyl-dimethylene-quinone** $(C_6H_5)_2C:C_6H_4:C(C_6H_5)_2$, orange needles, m.p. 239°–242°; the latter adds bromine with decoloration, eliminates iodine from HI, and is related to the *methylene-quinones* (B. **37,** 1463; **41,** 2746). Tetraphenyl-methylene-quinones are also produced by the condensation of two molecules diphenyl-ketene with one molecule quinone, with rejection of two molecules CO_2 from the unstable β-dilactones first formed. On treating the glycol with aniline salt or with phenol in glacial acetic acid we obtain **p$_2$-diamido-** and **p-dioxy-hexaphenyl-p-xylol** $H_2NC_6H_4.C(C_6H_5)_2C_6H_4C(C_6H_5)_2C_6H_4NH_2$, m.p. 358°, and $HOC_6H_4C(C_6H_5)_2C_6H_4C(C_6H_5)_2C_6H_4OH$, m.p. 304° (B. **37,** 2001).

III. C. **Tetraphenyl-methane** $C(C_6H_5)_4$, m.p. 282°, b.p. 431° with sublimation, is formed from the diazonium sulphate of p-amino-tetraphenyl-methane by boiling with alcohol, and also, in small quantities, by heating triphenyl-methane-azo-benzol to 100° (B. **36,** 1090). Also by transformation of triphenyl-chloro-methane with phenyl-magnesium chloride (B. **39,** 1463).

p-Amido- and **p-oxy-tetraphenyl-methane** $NH_2[4]C_6H_4C(C_6H_5)_3$, m.p. 245°, and $HO[4]C_6H_4C(C_6H_5)_3$, m.p. 282°, is easily obtained from triphenyl-carbinol in glacial acetic acid by heating with aniline chlorohydrate and phenol respectively, and concentrated sulphuric acid (B. **35,** 3018; **36,** 407; **37,** 659; A. **368,** 284).

p-Diphenyl-methyl-tetraphenyl-methane $(C_6H_5)_2CH[4]C_6H_4C(C_6H_5)_3$, m.p. 231°, is formed from triphenyl-carbinol, or its chloride, by reduction with zinc and stannous chloride, HCl, and glacial acetic acid; also from hexaphenyl-ethane and triphenyl-methyl by the action of HCl (B. **37,** 4790). Also synthetically by way of p-benzoyl-triphenyl-methane $C_6H_5COC_6H_4CH(C_6H_5)_2$, m.p. 166° (B. **41,** 2421).

IV. Homologous Di- and Poly-phenyl-paraffins.

Homologous series are derived from diphenyl-methane. Dismissing the substitutions in the benzene residues, this is attained by replacing the H atoms of the methylene residue by alkyl groups: diphenyl-methyl-, diphenyl-dimethyl-, diphenyl-ethyl-, diphenyl-propyl-methane, etc., denoted as "*gem-*" (*geminated*) *diphenyl-paraffins* (B. **81**, 2068); and again, it can be done by inserting new C atoms between the two benzene residues: ω,ω-diphenyl-ethane or dibenzyl, ω,ω-diphenyl-propane, ω,ω-diphenyl-butane, ω,ω-diphenyl-pentane, etc. The group of unsym. diphenyl-ethanes and the homologous gem-diphenyl-paraffins will receive first attention in the following paragraphs. Its members attach themselves in their behaviour to diphenyl-methane and its derivatives; at the same time they show in many ways their genetic relationship to the dibenzyl group. Compare benzilic acid, diphenyl-acetaldehyde, stilbene, tolane.

After these there will follow the important dibenzyl or sym. diphenyl-ethane group, and then the ω,ω-diphenyl, propane, butane, pentane, and hexane groups. The derivatives alkylised or phenylated in the benzene nuclei, or in the side chains connecting these, are included with the parent hydrocarbons of the individual groups; the saturated are followed by the unsaturated hydrocarbons.

A. *Gem-diphenyl-paraffins and their Derivatives* are, as a rule, formed (1) by the condensation of aldehydes, chlorinated aldehydes, glyoxylic acid, etc., with benzene hydrocarbons, phenols, or tertiary anilines, just as the diphenyl-methanes are produced by means of methylal, methylene iodide, etc.:

$$CH_2CHO + 2C_6H_6 \longrightarrow CH_3CH(C_6H_5)_2 + H_2O.$$

(2) Diphenyl-alkyl-carbinols are obtained by the condensation of benzo-phenone with magnesium-alkyl iodides or from phenyl-magnesium bromide with fatty-acid esters and chlorides (Grignard's reaction). The carbinols easily split off water and form gem-diphenyl-olefins, which are reducible by Na and alcohol to gem-diphenyl-paraffins:

$$(C_6H_5)_2CO \xrightarrow{CH_3MgI} (C_6H_5)_2C(OH)CH_3 \xleftarrow{CH_3CO_2R} 2C_6H_5MgBr$$
$$(C_6H_5)_2C(OH).CH_2CH_3 \longrightarrow (C_6H_5)_2C:CHCH_3 \longrightarrow C_6H_5CH_2.CH_2CH_3.$$

All the substances included in this class yield *benzo-phenone* or its derivatives when they are oxidised.

Unsym. diphenyl-ethane $(C_6H_5)_2CHCH_3$, b.p. 209° (145° at 13 mm.), is made from benzene and paraldehyde with cold sulphuric acid; also from ethidene chloride CH_3CHCl_2, sym. bromethyl-benzol $C_6H_5.CHBr.CH_3$, or styrol with benzene and Al_2Cl_6. Chromic acid oxidises it to benzo-phenone, with the elimination of the methyl group. Consult B. **27**, 3238. Nitric acid nitrates the side chains and the benzene residues of unsym. diphenyl-ethane. The products are: **diphenyl-ethylene-glycol mononitrate** $(C_6H_5)_2C(OH).CH_2(ONO)$, melting at 100°, **diphenyl-vinyl nitrite** $(C_6H_5)_2C{=}CH(ONO)$, melting at 86°, and a **dinitrite** melting at 148°–149°. The latter is probably a diphenyl-ethylene derivative. These three compounds have great crystallising power. They form yellow crystals, and when oxidised yield benzo-phenone (A. **288**, 330).

Unsym. phenol-phenyl-ethane $C_6H_5CH(CH_3)C_6H_4.OH$, melting at 58°, is produced when sulphuric acid acts upon phenol and styrol; the homologous phenols, naphthols, etc., behave similarly toward styrol (B. **24,** 3891). Unsym. **diphenol-ethane** $(C_6H_4OH)_2CHCH_3$, melting at 122°, can be obtained from aldehyde and phenol (B. **19,** 3009).

Unsym. p_2-tetramethyl-diamido-diphenyl-ethane $[(CH_3)_2NC_6H_4]_2CHCH_3$, m.p. 69°, is split up by nitrous acid with formation of p-nitro-dimethyl-aniline (C. 1899, II. 203; 1900, I. 252).

gem-Diphenyl-propane, -butane, -hexane, b.p.$_{10}$ 142°, 150°, 164°, from the corresponding olefins (see below) with Na and alcohol (C. 1902, II. 1209).

Diphenyl-methyl-, -ethyl-, -propyl-, -amyl-carbinol $(C_6H_5)_2C(OH)R$, m.p. 81°, m.p. 95°, b.p.$_{15}$ 185°, m.p. 47°, from benzo-phenone with alkyl-magnesium iodides or phenyl-magnesium bromide and fatty esters, by method 2 (see above). By distillation and dehydrating processes we obtain from these carbinols: **gem-diphenyl-ethylene, -propylene, -butylene, -hexylene,** b.p. 270°, 280°, m.p. 52°, 292°, 314°; unsym. diphenyl-ethylene is also formed from α-diphenyl-β-chlor-ethane (see below), and from unsym. dibromo-ethylene with benzene and $AlCl_3$. It easily splits off formaldehyde by auto-oxidation. Gem-diphenyl-propylene with Br immediately gives **α-diphenyl-β-bromo-propylene** $(C_6H_5)_2C:CBrCH_3$, m.p. 49° (B. **35,** 2646; **37,** 230, 1447; C. 1901, I. 1337; 1902, II. 1209). **o-Oxy-diphenyl-ethylene** $HO[_2]C_6H_4C(C_6H_5):CH_2$, b.p.$_{18}$ 167°, see B. **36,** 4002.

Several halogen derivatives of mono-substituted diphenyl-ethylenes of the general formula $\begin{matrix}C_6H_5-\\C_6H_4X\end{matrix}\!\!>\!C:C\!<\!\begin{matrix}H\\Hlg\end{matrix}$ occur in cis-trans-isomeric forms which can be transformed into each other by means of ultra-violet light (A. **342,** 1; B. **42,** 4865).

Unsym. diphenyl-monochloro-ethane $(C_6H_5)_2CH.CH_2Cl$ is an oil. **Diphenyl-dichloro-ethane** $(C_6H_5)_2CH.CHCl_2$, melting at 80°, and **diphenyl-trichloro-ethane** $(C_6H_5)_2CH.CCl_3$, melting at 64°, are obtained from mono-, di-, and trichloro-acetaldehyde (chloral) with benzene and sulphuric acid. Alkali, acting upon these substances, splits off hydrogen chloride, and the products are:

Unsym. diphenyl-ethylene, diphenyl-monochloro-ethylene $(C_6H_5)_2C:CHCl$, melting at 42° and boiling at 298°, and **diphenyl-dichloro-ethylene** $(C_6H_5)_2C:CCl_2$, melting at 80° and boiling at 316°, which is also found in the condensation products of chloral with benzene and aluminium chloride (B. **26,** 1955). If diphenyl-monochloro-ethane be heated alone it splits off hydrochloric acid and is rearranged to **stilbene.** The latter is similarly produced by the reduction and rearrangement of diphenyl-trichloro-ethane with zinc dust and alcohol. When diphenyl-monochloro-ethylene is heated with a sodium ethylate solution it is transformed into **tolane. Diphenyl-vinyl-ethyl ether** $(C_6H_5)C:CHOC_2H_5$ is formed simultaneously:

$$(C_6H_5)CH.CH_2Cl \xrightarrow{-HCl} C_6H_5.CH:CH.C_6H_5$$
$$(C_6H_5)_2CH:CHCl \xrightarrow{-HCl} H_6C_5.C:C.C_6H_5.$$

These transposition reactions have been extended to a series of substituted diphenyl-mono- and trichloro-ethanes and to diphenyl-monochloro-ethylene (A. **279,** 319; B. **26,** R. 270).

Unsym. diphenyl-ethylene-glycol $(C_6H_5)_2C(OH).CH_2OH$, m.p. 121°, is formed from glycolic ester or benzoyl-carbinol by transformation into phenyl-magnesium bromide. Similarly we obtain **diphenyl-propylene-glycol** $(C_6H_5)_2C(OH).CH(OH).CH_3$, m.p. 96°; **1, 1-diphenyl-glycerin** $(C_6H_5)_2C(OH)CH(OH).CH_2OH$, m.p. 158°; and **diphenyl-ethylene-chloro-hydrin** $(C_6H_5)_2C(OH).CH_2Cl$, m.p. 66°, from lactic ester, glyceric ester, and chloracetic ester with C_6H_5MgBr respectively. The latter, on heating with sodium ethylate, gives **diphenyl-ethylene oxide** $(C_6H_5)_2C.O.CH_2$, m.p. 56° (B. **39**, 1753, 2288).

On heating with 20 per cent. sulphuric acid, diphenyl-ethylene oxide, distilled in a vacuum, passes into **diphenyl-acetaldehyde** $(C_6H_5)_2CH.CHO$, b.p. 166°, oxime, m.p. 120°, which is also formed by saponification with glacial acetic acid and hydrochloric acid instead of diphenyl-vinyl alcohol.

The aldehyde in many respects behaves analogously to the oxymethylene derivatives—*e.g.* when it is oxidised it does not change to the acid, but splits off the CHO group and becomes benzo-phenone (B. **24**, 1780; **25**, 1781). Diphenyl-acetaldehyde is also formed from the hybro-benzoïns by dehydrating agents. Anhydrides of the hydro-benzoïns are formed at the same time:

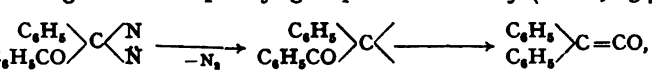
$$C_6H_5.CH.OH.CH.OHC_6H_5 \xrightarrow{-H_2O} (C_6H_5)_2CH.CHO.$$

This is due to an atomic rearrangement opposite to that of the transpositions of the unsym. diphenyl-chloro-ethanes and ethylenes just indicated. It reminds one of the pinacolin rearrangement of the pinacones.

Similarly we obtain from methyl- and ethyl-hydrobenzoïn $C_6H_5CH(OH).C(Alk)OHC_6H_5$: *α, α*-**diphenyl-propion-aldehyde** $(C_6H_5)_2C(CH_3).CHO$, b.p.$_{12}$ 176°, and *α, α*-**diphenyl-butyr-aldehyde** $(C_6H_5)_2C(C_2H_5).CHO$, b.p. 314° (C. 1907, I. 726).

Unsym. diphenyl-acetone $(C_6H_5)_2CH.COCH_3$, m.p. 45° and 61° (dimorphous), *oxime*, m.p. 164°, is formed on heating diphenyl-propylene-glycol with dilute HCl (B. **39**, 2302).

Diphenyl-ketene $(C_6H_5)_2C:CO$, b.p.$_{12}$ 146°, a reddish-yellow liquid solidifying in freezing mixture to straw-yellow crystals, is the first and most closely studied representative of the interesting class of the ketenes (Staudinger, 1905; cp. Vol. I.). It is formed by the action of zinc upon diphenyl-chloracetic acid chloride, or by the withdrawal of HCl from diphenyl-acetic acid chloride by means of tertiary bases (A. **356**, 51). Its easy formation by heating azi-benzile with rejection of N_2 and migration of a phenyl group is noteworthy (B. **42**, 2346):



a reaction which appears to correspond to the formation of stilbene from diphenyl-monochloro-ethylene, and of tetraphenyl-ethylene from benzo-pinacolin alcohol.

Diphenyl-ketene is more stable than the aliphatic representatives of this class of bodies, and shows no tendency towards polymerisation; but it shows greater reactivity. (1) With water it forms diphenyl-acetic acid or its anhydride. (2) With alcohols it forms diphenyl-

acetic ester. (3) With HCl it forms diphenyl-acetic acid chloride. (4) With NH_3, phenyl-hydrazin, and primary and secondary bases it forms the corresponding diphenyl-acetic acid derivatives. (5) With organic acids we obtain mixed acid anhydrides. (6) With sodium-malonic ester we obtain diphenyl-acetyl-malonic ester $(C_6H_5)_2CH.COCH(CO_2R)_2$. (7) With phenyl-magnesium bromide we obtain triphenyl-vinyl alcohol, $(C_6H_5)_2C:C.(OH)C_6H_5$. (8) With Schiff's bases it unites with formation of β-lactones :

$$(C_6H_5)_2C{=}CO+C_6H_5CH{=}NC_6H_5 \longrightarrow \begin{matrix}(C_6H_5)_2C{=}CO\\ C_6H_5CH{=}NC_6H_5\end{matrix}$$

(9*a*) With $\alpha\beta$-unsaturated aldehydes and ketones we obtain, on heating the components in indifferent solvents, unstable β-lactones which, in the nascent state, decompose into CO_2 and multiple unsaturated hydrocarbons (B. **42**, 4249) :

$$(C_6H_5CH:CH)_2CO+(C_6H_5)_2C:CO \longrightarrow (C_6H_5CH:CH)_2C\begin{matrix}\diagup C(C_6H_5)_2\\ O\text{———}\diagdown CO\end{matrix}$$

$$(C_6H_5CH:CH)_2C:C(C_6H_5)_2, \quad -2CO_2$$

(9*b*) The quinones react like the $\alpha\beta$-unsaturated ketones ; according to the quantities used, mono- or dilactones of β-oxy-acids are formed, while the latter decompose at once into $2CO_2$ and tetraphenyl-dimethylene-quinones :

$$\begin{matrix}CO.C(C_6H_5)_2\\ |\text{———}O\end{matrix}\diagdown C_6H_4\diagup\begin{matrix}C(C_6H_5)_2.CO\\ O\text{———}|\end{matrix} \xrightarrow{-2CO_2} (C_6H_5)_2C:C_6H_4:(C_6H_5)_2.$$

The monolactones can be isolated, and are only split up into CO_2 and diphenyl-quino-methanes on heating.

o-Substituents depress the reactivity of the quinone groups, so that chloranile and anthraquinone no longer unite with diphenyl-ketene (A. **380**, 243).

Diphenyl-acetic acid $(C_6H_5)_2CH.CO_2H$ is formed from its nitrile by saponification ; by reducing benzilic acid with hydriodic acid and phosphorus in glacial acetic acid (A. **275**, 84) ; and from diphenyl-dichloro-ethylene by heating to 180° with Na alcoholate, a reaction which may be generalised (A. **306**, 79). The acid melts at 146°. When oxidised with a chromic acid mixture it yields benzo-phenone ; and when heated with soda-lime we get diphenyl-methane. Its *ethyl ester* melts at 58° ; the *methyl ester* at 60° ; and the *chloride* at 57°.

Diphenyl-aceto-nitrile $(C_6H_5)_2CH.CN$ results when diphenyl-bromo-methane is heated with $Hg(CN)_2$, or by the condensation of mandelic nitrile, $C_6H_5.CH(OH)CN$, and benzene with tin tetrachloride (B. **25**, 1615). It melts at 72° and boils at 184° (at 12 mm.). The hydrogen of its CH group is readily replaced by the benzene residue, but not by alkyls (A. **275**, 87). Iodide, acting upon its sodium derivatives, produces tetraphenyl-succino-nitrile.

p_2-Ditolyl-, -dianisyl-, and **-diphenetyl-acetic acid,** m.p. 144°, 110°, and 114° (A. **306**, 81).

Tetranitro-diphenyl-acetic acid $\begin{matrix}C_6H_3(NO_2)_2\\ C_6H_3(NO_2)_2\end{matrix}\diagdown CH.CO_2H$. The *ethyl ester* is derived from dinitro-phenyl-aceto-acetic ester and dinitro-

phenyl-malonic ester by the action of o, p-dinitro-bromo-benzol, the group $CO.CH_3$ (and $CO_2.C_2H_5$) being replaced. It may be similarly prepared from dinitro-phenyl-acetic ester by the introduction of the dinitro-phenyl residue. It melts at 154°. Alcoholic potash or soda converts the ester, by the substitution of the hydrogen of the CH group, into brilliant metallic salts, dissolving in alcohol and water, with a dark-blue colour. Compare tetranitro-phenyl-methane $[(C_6H_3NO_2)_2]CH_2$ and trinitro-triphenyl-methane $(C_6H_4NO_2)_3CH$ (B. **21**, 2476).

p_2-Diamido-diphenyl-acetic acid $[NH_2C_6H_4]_2CHCO_2H$, m.p. 234°, is formed by the transposition of dianilido-acetic acid $(C_6H_5NH)_2CHCO_2H$, on heating with aniline and its chlorohydrate (B. **41**, 3019, 3031).

p-Oxy-diphenyl-acetic acid, m.p. 173°, from mandelic acid or its nitrile with phenol and sulphuric acid (73 per cent.), besides **o-oxy-diphenyl-acetic lactone** $C_6H_5CH\langle{}^{C_6H_4}_{CO}\rangle O$, m.p. 114°. The latter yields a bromine derivative easily transformed into o-oxy-diphenyl-glycocoll $HOC_6H_4C(C_6H_5)(NH_2)COOH$ (B. **31**, 2812).

Tetra-oxy-diphenyl-acetic acid $COOH.CH[C_6H_3(OH)_2]_2$ has been obtained by the condensation of chloral with resorcin by means of potassium bisulphate. It has a yellow colour. It dissolves in cold alkalies with a red colour, and forms a *triacetyl derivative* melting at 152° (B. **29**, R. 776; C. 1897, II. 739).

Benzilic acid, *diphenyl-glycolic acid* $(C_6H_5)_2C(OH).CO_2H$, m.p. 150°, is produced by a molecular rearrangement of benzile (*q.v.*) when digested with alcoholic potassium hydroxide, and from diphenyl-acetic acid by the action of bromine and boiling with water. We can prepare it better by the action of aqueous potash and air upon benzoin (B. **19**, 1868; C. 1902, I. 1012):

$$C_6H_5COCOC_6H_5 \xrightarrow{H_2O} (C_6H_5)_2C(OH)COOH.$$

When heated above its melting-point, benzilic acid takes on a blood-red colour, and dissolves with the same colour in sulphuric acid. Diphenylene-diphenyl-ethane derivatives are produced by the action of concentrated sulphuric acid upon benzilic acid (B. **29**, 734).

With phosphorus chlorides benzilic acid yields **diphenyl-chloracetic acid** $(C_6H_5)_2CClCO_2H$, m.p. 119° with decomposition (B. **36**, 145), and **diphenyl-chloracetic acid chloride,** m.p. 50° (A. **356**, 72); with P_2O_5 or $COCl_2$ and pyridin we obtain **benzilide** $(C_6H_5)_2C\langle{}^{O.CO}_{CO.O}\rangle C(C_6H_5)_2$, m.p. 196° (B. **35**, 3642). It yields diphenyl-acetic acid when heated with hydriodic acid and phosphorus. On distilling its barium salt it breaks up into carbon dioxide and benzo-hydrol; oxidation yields benzo-phenone.

p-Tolilic acid $(CH_3C_6H_4)_2$: $C(OH)COOH$; **anisilic acid** $(CH_3OC_6H_4)_2C(OH)COOH$; **cuminilic acid** $(C_3H_7C_6H_4)_2C(OH)COOH$; and **hexa-methoxy-benzilic acid** $[(CH_3O)_3C_6H_2]_2C(OH)COOH$ are prepared, like benzilic acid, from their corresponding substituted benziles.

β,β-Diphenyl-propionic acid $(C_6H_5)_2CH.CH_2.COOH$ is a homologue of diphenyl-acetic acid. It melts at 149°. It is formed by the addition of phenyl-magnesium bromide to cinnamic acid ester (C. 1905, I.

522). This is accomplished by means of sulphuric acid, just as phenol-phenyl-ethane is obtained from styrol and phenol, or benzene is attached to cinnamic acid. The continued action of the sulphuric acid leads to a condensation to γ-phenyl-hydrindone. The α-bromo-β,β-diphenyl-propionic acid, m.p. about 164°, and especially its potassium salt, decompose on evaporating their aqueous solution into CO_2, HBr, and stilbene, a reaction corresponding to the formation of this hydrocarbon from diphenyl-monochloro-ethylene (C. 1905, II. 1022).

Phenyl-tolyl-, phenyl-xylyl-propionic acids, etc., are prepared just like diphenyl-propionic acid (B. **26,** 1579). Potassium permanganate oxidises these acids to benzo-phenone, phenyl-tolyl-ketone, phenyl-xylyl-ketone, etc.

γ, γ-Diphenyl-butyric acid $(C_6H_5)_2CHCH_2CH_2COOH$, m.p. 107°, from **γ-phenyl-butyro-lactone** or phenyl-iso-crotonic acid, with benzene and $AlCl_3$ (C. 1907, II. 2045).

α, α-Diphenyl-propionic acid $(C_6H_5)_2C(CH_3)CO_2H$, m.p. 173°, and its homologues are obtained by condensation of phenyl-pyro-racemic acid with benzene and its homologues by means of concentrated sulphuric acid (B. **14,** 1595). On heating with concentrated sulphuric acid they split off CO and yield diphenyl-carbinols, which in turn easily decompose into water and unsym. diaryl-ethylenes (B. **38,** 839).

β-Phenyl-cinnamic acid $(C_6H_5)_2C : CH.CO_2H$, m.p. 162°, is formed, like β-alkyl-cinnamic acids, from the condensation product of benzo-phenone with bromacetic ester and zinc (B. **40,** 4537; **41,** 324), and from α-bromo-β, β-diphenyl-propionic acid with alcoholic potash (C. 1905, I. 522).

γ-Diphenyl-itaconic acid $(C_6H_5)_2C : C(COOH).CH_2.COOH$, m.p. 169° with decomposition, is obtained by the condensation of benzo-phenone with succinic ester through the agency of sodium ethylate. The acid, on heating under reduced pressure, gives an anhydride, m.p. 147°–150°, whose soda solution on acidulation yields **diphenyl-citraconic acid** $(C_6H_5)_2CHC(COOH) : CHCOOH$, m.p. 110°–115° with decomposition. This acid is condensed by sulphuric acid to phenyl-indone-acetic acid. With bromine it gives **γ-diphenyl-bromo-paraconic acid** $(C_6H_5)_2\overline{C.CBr(COOH).CH_2.COO}$, which, on heating with water, passes into **γ-diphenyl-aconic acid,** m.p. 139°, and further, with rejection of CO_2, **diphenyl-croto-lactone** $(C_6H_5)_2\overline{C.CH : CH.COO}$, m.p. 131° (A. **308,** 89). **γ-Diphenyl-α,β-dichloro-crotonic acid** $(C_6H_5)_2CH.CCl : CCl$ COOH, m.p. 152°, is formed from muco-chloric acid chloride (see Vol. I.), benzene, and $AlCl_3$ (C. 1897, II. 570). **γ-Diphenyl-acetacrylic ester** $(C_6H_5)_2C : C(COCH_3)COOC_2H_5$, m.p. 76°, from benzo-phenone chloride and cu-aceto-acetic ester, yields by ketone splitting **diphenyl-butenone** $(C_6H_5)_2C : CHCOCH_3$, m.p. 33°, b.p.$_{18}$ 190° (B. **32,** 1433), and homologues are formed from triphenyl-chloro-methane and alkyl-magnesium haloids (B. **39,** 2957).

Triphenyl-acetaldehyde $(C_6H_5)_3C.CHO$, m.p. 223°, from triphenyl-magnesium chloride and formic acid ester.

Triphenyl-methyl-ethyl-ketone $(C_6H_5)_3C.COC_2H_5$, m.p. 104°, from triphenyl-acetic acid chloride and C_2H_5MgI (B. **43,** 1137).

Triphenyl-acetic acid $(C_6H_5)_3C.COOH$ is a very feeble acid. It melts

at 264°, and decomposes into triphenyl-methane-carboxylic acids. It is made by the action of benzene and aluminium chloride upon trichloracetic acid, and when carbon dioxide is conducted over potassium triphenyl-methane at 200°. The *nitrile* is produced by the interaction of triphenyl-chloro- or bromo-methane and mercuric cyanide $Hg(CN)_2$ (A. **194**, 260; B. **28**, 2782), or by deamidising hydrocyano-para-rosanilin (B. **26**, 2225).

p_3-Triamido-triphenyl-acetic nitrile, *hydrocyano-para-rosanilin,* results upon digesting para-rosanilin salts with alcohol and potassium cyanide. Hydrocyano-rosanilin is similarly obtained from rosanilin salts. According to Hantzsch, quinoid ammonium cyanides are first generated, and these transpose themselves into nitriles in the solution itself (B. **33**, 287):

$$(NH_2.C_6H_4)_2C:C_6H_4:NH_2CN \longrightarrow (NH_2.C_6H_4)_2C(CN).C_6H_4.NH_2.$$

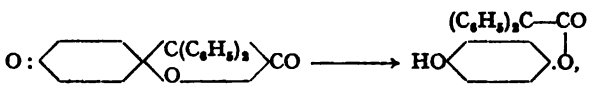
The chlorohydrates of these hydrocyano-compounds decompose on heating into HCl, HCN, and the rosanilin salts.

Substituted triphenyl-acetic acids, especially phenol derivatives, are easily obtained from benzilic acid with phenols by condensation with tin tetrachloride (B. **34**, 3080; **37**, 664; **40**, 4060):

$$(C_6H_5)_2C\langle^{OH}_{COOH} + C_6H_5OH \xrightarrow{SnCl_4} (C_6H_5)_2C\langle^{C_6H_4OH}_{COOH}.$$

Diphenyl-p-tolyl-acetic acid $CH_3[4]C_6H_4(C_6H_5)_2CCOOH$, m.p. 205°. **p-Tritolyl-acetic acid** $(CH_3C_6H_4)_3C.CO_2H$, m.p. 227°. **p-Oxy-triphenyl-acetic acid** $HO[4]C_6H_4(C_6H_5)_2CCOOH$, m.p. 212°. **m-** and **p-Cresol-diphenyl-acetic acid lactone** $O[2]C_6H_3(CH_3)[1]C(C_6H_5)_2CO$, m.p. 126° and 130°. **o-** and **m-Xylenyl-diphenyl-acetic acid lactone,** m.p. 178° and 170°. **Thymoyl-** and **carvacroyl-diphenyl-acetic acid** $HO[4]C_6H_2(CH_3)(C_3H_7)[1]C(C_6H_5)COOH$, etc.

Diphenyl-methyl-quinol-carboxylic acid lactone (formula, see below), colourless crystals, m.p. 143°, is formed by condensation of diphenyl-ketene with excess of quinone. On heating, it decomposes into CO_2 and diphenyl-quino-methane. As a quinol derivative it shows the transposition into benzene derivatives with migration of the alkyl group characteristic of these compounds; thus, the above β-lactone on illumination in the solid state or in boiling benzene solution passes into the isomeric **2, 5-dioxy-triphenyl-acetic acid lactone,** m.p. 196°:



which has also been obtained synthetically from hydroquinone and benzilic acid by means of $SnCl_4$ (A. **380**, 248).

B. *Sym. Diphenyl-ethane Group.*—**Dibenzyl,** *sym. diphenyl-ethane* $C_6H_5.CH_2.CH_2.C_6H_5$, m.p. 52° and b.p. 284°, is prepared (1) by the action of sodium or copper upon benzyl chloride $C_6H_5.CH_2Cl$, or (2) of $AlCl_3$ upon benzene and ethylene chloride or ω-chlorethyl-benzene (A. **235**, 155); and (3) by heating its oxygen derivatives, benzoïn and benzile, and from the unsaturated hydrocarbons tolane and stilbene

by reduction with Na and alcohol (B. **35,** 2647), HI, or H and Ni at 220° (C. 1908, I. 469). Finally, it can be obtained (4) by oxidation of toluol with potassium persulphate (B. **32,** 2531). It forms stilbene and tolane when heated to 500°. Chromic acid and potassium permanganate oxidise it directly to benzoic acid. It yields two dinitro-compounds by nitration.

p, p-Dinitro-dibenzyl has also been obtained by the action of stannous chloride upon p-nitro-benzyl chloride. It melts at 181° (A. **238,** 272 ; B. **20,** 909). Also by the action of cold methyl-alcoholic potash upon p-nitro-toluol (C. 1908, I. 642). **o, o-Dinitro-dibenzyl,** m.p. 122° (C. 1910, II. 570).

p_2-Diamido-dibenzyl can be used for the preparation of tetrazo-dyes in the same way as diamido-stilbene (C. 1899, I. 1171).

o_2-Diamido-dibenzyl, m.p. 68°, by reduction of o_2-diamido-stilbene. On heating its chlorohydrate it gives **imido-dibenzyl** $\begin{matrix}CH_2C_6H_4\\CH_2C_6H_4\end{matrix}\!\!>\!NH$, m.p. 110°, which contains a seven-membered ring (A. **305,** 96).

Homologues of Dibenzyl.—**o_2, m_2,** and **p_2-Dimethyl-dibenzyl,** m.p. 66°, 82°, and 296°, are produced by oxidation of o-, m-, and p-xylol with potassium persulphate (B. **32,** 2531).

α, β-Diphenyl-propane $C_6H_5CH(CH_3)CH_2C_6H_5$, b.p.$_{28}$ 167°, by reduction of α-methyl-stilbene. **α, β-Diphenyl-iso-butane** $C_6H_5CH_2C(CH_3)_2C_6H_5$, from iso-butylene bromide, benzene, and $AlCl_3$ (C. 1901, II. 202).

α,β-Phenyl-tolyl-propane $C_6H_5CH(CH_3)CH_2C_6H_4CH_3$, and **α,β-phenyl-xylyl-propane,** are produced when concentrated sulphuric acid acts upon styrol in the presence of xylene or trimethyl-benzene. The homologous benzenes, containing a methyl group, attach themselves to the unsaturated linkage in the styrol (B. **23,** 3269).

Diphenyl-dimethyl-ethane $C_6H_5.CH(CH_3)CH(CH_3)C_6H_5$, melting at 123°, is formed when sodium or zinc dust acts upon a β-haloid ethyl-benzene $C_6H_5.CHX.CH_3$ (B. **26,** 1710); also from ethyl-benzol with persulphate (B. **32,** 434).

Stilbene, toluylene, *sym. diphenyl-ethylene* $C_6H_5.CH : CH.C_6H_5$, melting at 124° and boiling at 306°, crystallises in large, glistening (στίλβειν, to glisten) monoclinic leaflets or prisms. It is obtained by a great variety of methods. It belongs to a long-known class of aromatic substances (Laurent, 1844). It is produced:

(1) By distilling benzyl sulphide and disulphide.

(2) By heating polymeric thio-benzaldehyde to 150°, or by distilling trithio-benzaldehyde with metallic copper (B. **25,** 600).

(3) By the action of metallic sodium upon benzaldehyde or benzal chloride.

(4) From benzaldehyde and phenyl-acetic acid, instead of the expected phenyl-cinnamic acid (*J. pr. Ch.* 2. **61,** 169).

(5) By magnesium organic syntheses stilbene and its homologues are formed from benzyl-magnesium chloride with benzaldehydes or aromatic ketones, the benzyl-aryl-carbinols formed as primary products splitting off water (B. **37,** 453, 1447).

(6) By heating iso-nitro-benzyl cyanide $C_6H_5C(:NOOH)CN$ with soda to high temperatures, whereby phenyl-iso-nitro-methane is first formed, which splits off sodium nitrite and forms stilbene (B. **38,** 502).

(7) From benzal-azin $C_6H_5CH : N.N : CHC_6H_5$ and phenyl-diazo-methane $C_6H_5CHN_2$, by heating and rejection of nitrogen.

(8) From chlorinated, asymmetrical diphenyl-ethane derivatives —*e.g.* $(C_6H_5)_2CH.CH_2Cl$, $(C_6H_5)_2CH.CCl_3$—by a rearrangement caused by heat or zinc dust (B. **7**, 1409; *J. pr. Ch.* 2, **47**, 44).

(9) By the action of metallic copper, potassium sulphydrate (B. **24**, 1776), or potassium cyanide (B. **11**, 1219) upon stilbene dihalides.

(10) An interesting method for its production is that of distilling fumaric and cinnamic phenyl esters (B. **18**, 1945):

$$\underset{\text{Diphenyl-fumaric ester}}{C_6H_5OCOCH : CH.COOC_6H_5} \xrightarrow{-C_2O} \underset{\text{Phenyl-cinnamic ester}}{C_6H_5.CH : CH.CO.OC_6H_5} \xrightarrow{-CO_2} \underset{\text{Stilbene.}}{C_6H_5.CH : CH.C_6H_5}$$

Compare also the decomposition of chloro-benzyl-desoxy-benzoïn in benzoyl chloride and stilbene.

As an unsaturated compound, stilbene can occur in a second stereo-isomeric form. This iso-stilbene is a liquid, b.p.$_{12}$ 143°, and has a pleasant flower-like odour. It is formed by the reduction of tolane or iso-bromo-stilbene with zinc dust and alcohol (A. **342**, 208), also from the ordinary stilbene by illuminating by ultra-violet light in benzene solution (B. **42**, 4871), besides the polymeric distilbene $C_{28}H_{24}$, m.p. 163° (B. **35**, 4129). By traces of iodine or bromine, distillation at ordinary pressure, or vapours of fuming nitric acid, it passes into the stable solid stilbene. Its formation from tolane indicates for iso-stilbene the cis-configuration $\begin{matrix}HC.C_6H_5\\HC.C_6H_5\end{matrix}$, whereas $\begin{matrix}HC.C_6H_5\\C_6H_5CH\end{matrix}$ represents the ordinary stilbene as a trans-configuration.

When heated with hydro-iodic acid stilbene yields dibenzyl. The addition of halogens produces stilbene dihaloids, the haloid esters of the hydro-benzoïns. Chromic acid oxidises stilbene to benzaldehyde and benzoic acid. *Thionessal*, tetraphenyl-thiophene (*q.v.*), is produced when stilbene is heated for several hours at 250°, together with sulphur. Phenanthrene is formed when stilbene is heated.

With N_2O_3 and N_2O_4 stilbene combines to form $C_{14}H_{12}(N_2O_3)$ and $C_{14}H_{12}(N_2O_4)$; the former, on boiling with glacial acetic acid, is partly decomposed and converted into the latter, which is to be regarded as **diphenyl-dinitro-ethane** $C_6H_5CH(NO_2).CH(NO_2)C_6H_5$, α-mod., m.p. 236° with decomposition, β-mod., m.p. 150°–152° (B. **34**, 3536).

On treating with alkali it splits off one molecule of nitrous acid and passes into **7-nitro-stilbene** $C_6H_5CH : C(NO_2)C_6H_5$, m.p. 75°, which is also obtained by the condensation of phenyl-nitro-methane and benzaldehyde by means of aliphatic base (B. **37**, 4509), and by heating with methyl-alcoholic potash and then with HCl through a number of intermediate products into the isomeric benzyl-monoxime $C_6H_5COC(NOH)C_6H_5$ (A. **355**, 269).

α-Methyl-stilbene $C_6H_5C(CH_3) : CHC_6H_5$, m.p. 83°, b.p.$_{26}$ 183°, and **α-ethyl-stilbene,** m.p. 57°, b.p. 296°, from desoxy-benzoïn with CH_3MgI and C_2H_5MgI; also from aceto-phenone with $C_6H_5CH_2MgCl$ (B. **37**, 457, 1450; C. 1904, II. 1038).

Stilbenes having the substituents in the benzene nucleus are obtained from substituted benzyl and benzal chlorides; also by condensation of substituted benzaldehydes with phenyl-acetic acid; or of o-chloro-benzal chloride with copper.

o, o-Dichloro-stilbene $(Cl.C_6H_4.CH)_2$, m.p. 97°; and chloro-nitro-benzyl chloride and alcoholic potash give rise to **dichloro-nitro-stilbene,** m.p. 294° (B. **25,** 79; **26,** 640).

o, p-Dinitro-stilbene $(NO_2)_2[2, 4]C_6H_3CH : CHC_6H_5$, m.p. 140°, from benzaldehyde and o, p-dinitro-toluol by means of piperidin, give by partial reduction with ammonium sulphide **o-nitro-p-amido-stilbene,** m.p. 111°, and with stannous chloride **o-amido-p-nitro-stilbene,** m.p. 143°, and further **o, p-diamido-stilbene,** m.p. 120° (B. **34,** 2842).

The action of alcoholic potash upon o- and p-nitro-benzyl chlorides gives rise to two physical isomerides in each case: two **o, o-dinitro-stilbenes,** melting at 126° and 196° respectively, and two **p, p-dinitro-stilbenes,** melting at 210°–216° and 280°–284° (B. **21,** 2072; **23,** 1959; **26,** 2232), which yield corresponding diamido-stilbenes upon reduction.

p_2-Dinitro-stilbene-disulphonic acid is formed by the oxidation of p-nitro-toluol-sulphonic acid with alkaline hypochlorite; oo'-dinitro-dibenzyl-disulphonic acid is first formed, and on further oxidation p-nitro-benzal-dehydro-o-sulphonic acid (C. 1898, II. 94; C. 1900, I. 1085).

oo'-Diamido-stilbene, melting (cis-) at 123° and (trans-) at 168°, changes to *indol* on heating equivalent quantities of the hydrochloride and base; aniline is eliminated (B. **28,** 1411; but see o_2-Diamido-dibenzyl). The disulphonic acid of **p_2-diamido-stilbene** (melting at 227°), by diazotising and combining with phenol, passes into a tetrazo-compound, *brilliant yellow*. The mono-ethyl derivative $\begin{matrix}CH.C_6H_3(SO_3H)N : NC_6H_4OH\\ \|\\ CH.C_6H_3(SO_3H)N : NC_6H_4OC_2H_5\end{matrix}$ of the latter is the substantive cotton-dye *chrysophenin* (B. **27,** 3357). See B. **22,** R. 311 (cp. benzidin dyes), for additional dye-substances. On the electrolytic reduction of nitro-stilbenes to cyclic azoxy- and azo-stilbenes, see C. 1903, I. 1414.

o-Oxy-stilbene, m.p. 147° (B. **42,** 825).

p-Oxy-stilbene, m.p. 189°, see A. **349,** 107.

o, o'-Dioxy-stilbene, m.p. 92°, is formed with other products from salicyl aldehyde on boiling with zinc dust and glacial acetic acid (B. **24,** 3175).

p_2-Dioxy-stilbene, m.p. 281°, is obtained as unsym. diphenol-trichloro-ethane $(HO[4]C_6H_4)_2CHCCl_3$, the condensation product of phenol and chloral, by treatment with zinc dust or iron powder. By attaching bromine at low temperatures it gives p_2-dioxy-stilbene dibromide, possessing the character of a pseudo-phenol-alcohol bromide. On treatment with sodium acetate it splits off 2HBr and yields **stilbene-quinone,** $O : C_6H_4 : CH.CH : C_6H_4 : O$, bright-red crystals, which can also be obtained direct from the p_2-dioxy-stilbene by oxidation with PbO_2 or $FeCl_3$, and resembles in its chemical behaviour the simple methylene-quinones (A. **335,** 157; B. **39,** 3490). At higher temperatures chlorine and bromine act upon p_2-dioxy-stilbene as substituents, forming tetrachloro- and tetrabromo-p_2-dioxy-stilbene dichloride and dibromide respectively, which, on treatment with alkali, pass into **tetrabromo-** and **tetrachloro-stilbene-quinone** $O : (C_6Cl_2H_2) : CH.CH : (C_6Cl_2H_2) : O$. These products are sparsely soluble and resemble phosphorus (A. **325,** 19).

3, 4-Methylene-dioxy-stilbene $CH_2O_2C_6H_3CH : CHC_6H_5$, m.p. 96°, from piperonal and benzyl-magnesium chloride (B. **37**, 1431).

Tolane, *diphenyl-acetylene* $C_6H_5.C : C.C_6H_5$, m.p. 60°, is produced from stilbene dibromide on boiling with alcoholic potash, and, further, together with diphenyl-vinyl ether, on treating unsym. diphenyl-chloro-ethylene $(C_6H_5)_2C : CHCl$ with sodium alcoholate.

The latter method proceeds more smoothly with the substituted tolanes. **Dimethyl-tolane,** m.p. 136°, and **dimethoxy-tolane,** m.p. 145°, are obtained from ditolyl- and dianisyl-chloro-ethylene.

o, o'-Dichloro-tolane, m.p. 89°, is made from o, o'-dichloro-stilbene dichloride.

Tetrachloro-p-dioxy-tolane, m.p. 226°, see A. **338**, 236.

The tolanes absorb two and four halogen atoms, the products being tolane di- and tetrachlorides (*q.v.*). The elements of water are taken up by the action of glacial acetic acid and sulphuric acid, with the formation of desoxy-benzoïns (below) (cp. Vol. I.).

The action of nitrous acid gas upon tolane produces α- and **β-diphenyl-dinitro-ethylene** $C_6H_5C(NO_2) : C(NO_2)C_6H_5$, m.p. 186°–187° and 105°–107° (B. **34**, 619). **p_2-Diamido-tolane,** m.p. 235°, and transformation products, see A. **325**, 67.

Alcohol and Ketone Derivatives of Dibenzyl.

C_6H_5CHOH	C_6H_5CO	C_6H_5CHOH	C_6H_5CO	C_6H_5CO
$C_6H_5CH_2$	$C_6H_5\dot{C}H_2$	$C_6H_5\dot{C}HOH$	$C_6H_5\dot{C}HOH$	$C_6H_5\dot{C}O$
Stilbene hydrate	Desoxy-benzoïn	Hydro-benzoïn	Benzoïn	Benzile.

Stilbene hydrate, *benzyl-phenyl-carbinol* $C_6H_5.CH(OH).CH_2.C_6H_5$, m.p. 62°, results upon reducing desoxy-benzoïn with sodium amalgam, and from the action of benzaldehyde upon benzyl-magnesium chloride. Similarly, **benzyl-phenyl-methyl-carbinol** $C_6H_5.C(OH)(CH_3).CH_2C_6H_5$, m.p. 51°, b.p.$_{15}$ 175°, is obtained from benzyl-magnesium chloride with aceto-phenone, or from desoxy-benzoïn with CH_3MgI; the latter carbinol splits off water with greater difficulty than does the former (B. **37**, 456, 1450).

Desoxy-benzoïn, *phenyl-benzyl-ketone* $C_6H_5.CO.CH_2.C_6H_5$, m.p. 60° and b.p. 314°. It is obtained by distilling a mixture of calcium benzoate and calcium α-toluate; also by the action of $AlCl_3$ upon a mixture of alpha-toluic chloride; by reducing benzoïn with zinc and hydrochloric acid (B. **21**, 1296; **35**, 912); from chloro-benzile and benzile (B. **26**, R. 585) by the action of hydriodic acid or zinc and HCl; and by heating monobromo-stilbene with water to 180°–190°. One H atom of its CH_2 group can be replaced by sodium and alkyls, but not the second (B. **21**, 1297; **23**, 2072). *Methyl-, iso-butyl-, cetyl-desoxy-benzoïn* melt at 58°, 78°, and 76° (B. **25**, 2237).

Its *oxime* melts at 98°. *Iso-nitroso-desoxy-benzoïn,* produced by N_2O_3, is identical with α-benzile-monoxime. Hydriodic acid converts desoxy-benzoïn into dibenzyl; see also *stilbene hydrate.*

The nitration of desoxy-benzoïn produces **o-nitro-desoxy-benzoïn** $C_6H_4(NO_2)CH_2.CO.C_6H_5$, which, upon reduction, yields α-phenyl-indol $C_6H_4\langle\begin{matrix}CH\\NH\end{matrix}\rangle C.C_6H_5$. **Desoxy-toluoïn** $CH_3.C_6H_4.CH_2.CO.C_6H_4.CH_3$,

and **desoxy-anisoïn** $CH_3O.C_6H_4.CH_2.CO.C_6H_4.OCH_3$, are formed from the corresponding tolanes (A. **279,** 335, 339) (above). $CSCl_2$, or carbon disulphide, and caustic potash, convert the desoxy-benzoïns into *desaurins*, which form brilliant golden-yellow needles. They dissolve in sulphuric acid with a violet-blue colour. The exact constitution of these bodies is not yet known. The simplest desaurin very probably has the composition $C_6H_5COC(CS)C_6H_5$ (B. **25,** 1731, 2239). Cp. B. **37,** 1599. **Mono-** and **polyoxy-desoxy-benzoïns,** see M. **26,** 927.

Hydro-benzoïn, *toluylene-glycol* $C_6H_5.CH(OH)CH(OH)C_6H_5$, has two asymmetric C atoms, and occurs in two optically inactive modifications (A. **259,** 100) : *hydro-benzoïn*, m.p. 134°, and *iso-hydro-benzoïn*, m.p. 119°. The latter has been resolved into two optically active components (see below). Both are produced, together with benzyl alcohol, when zinc and alcoholic hydrochloric acid act upon oil of almonds, or when the latter is treated with sodium amalgam, or in the electrolytic reduction of benzaldehyde (B. **29,** R. 229). Both are also obtained from stilbene bromide or chloride on converting the latter by silver acetate or benzoate into esters, and saponifying these with alcoholic ammonia. With potassium acetate, iso-hydro-benzoïn is almost the sole product. Hydro-benzoïn predominates (with a little iso-hydro-benzoïn) when sodium amalgam acts on benzoïn. This is also the best method for its preparation (A. **248,** 36).

Hydro-benzoïn dissolves with difficulty in water, crystallises in rhombic plates, melting at 134°, and sublimes without decomposition. The *diacetate* is obtained from benzaldehyde and acetyl chloride by means of zinc dust (B. **16,** 636) ; it melts at 134°.

Iso-hydro-benzoïn is more readily soluble in water. It crystallises in prisms which contain water of crystallisation and rapidly effloresce on exposure. Its *diacetate* is dimorphous, and crystallises in shining leaflets, melting at 118°, or in rhombic prisms, melting at 106°.

Dimolecular *anhydrides* $\begin{matrix} C_6H_5CH.O.CH.C_6H_5 \\ | \\ C_6H_5.CH.O.CH.C_6H_5 \end{matrix}$ (?), melting at 132° and 102°, are obtained, together with diphenyl-acetaldehyde $(C_6H_5)_2CH.CHO$, from both hydro-benzoïns by the action of sulphuric acid or P_2O_5.

By crystallisation from ether iso-hydro-benzoïn has been resolved into enantiomorphous dextro- and lævo-rotatory crystals (B. **30,** 1531). Chromic acid or potassium permanganate changes both hydro-benzoïns into benzaldehydes, and nitric acid converts them into benzoïn (B. **24,** 1776). PBr_5 changes both to the same **stilbene dibromide** $C_6H_5.CHBr.CHBr.C_6H_5$, melting at 237°, which has also been made by the action of bromine upon stilbene and dibenzyl. Stilbene and bromine yield not only the body (the α-) melting at 237°, but also a β-variety, melting at 110°. This is more readily soluble. It passes into the higher-melting variety under the influence of heat, and this again reverts by alcoholic potash into *liquid* monobromo-stilbene, whereas the β-modification by similar treatment changes to a *solid* monobromo-stilbene (B. **28,** 2693). Both hydro-benzoïns are changed by PCl_5 into α- and **β-stilbene dichloride,** melting at 192° and 93°. The α-compound is also produced when chlorine acts upon stilbene dissolved in chloroform. When heated to 200° the β- passes into the α-variety.

Diphenyl-oxethylamine $C_6H_5.CH(OH)CH(NH_2)C_6H_5$, melting at 163°, and **iso-diphenyl-oxethylamine,** melting at 129°, are produced together by the reduction of benzoïn-oxime, also from benzaldehyde and benzylamine, as well as by the condensation of benzaldehyde and glycocoll, together with phenyl-α-amido-lactic acid. This last reaction is explained by the condensation of benzaldehyde with benzylideneglycocoll in two directions according to the following scheme :

$$\text{I. } \begin{matrix} C_6H_5CH:NCHCOOH \\ HO.\dot{C}HC_6H_5 \end{matrix} \longleftarrow C_6H_5CH:NCH_2COOH \longrightarrow \begin{matrix} C_6H_5CHN:CHCOOH \\ C_6H_5\dot{C}HOH \end{matrix} \text{ II.}$$

I. is split up into benzaldehyde and phenyl-amido-lactic acid; II. into glyoxylic acid and diphenyl-oxethylamine. The two isomeric diphenyl-oxethylamines can be separated by means of their benzylidene compounds. Nitrous acid converts them both into iso-hydro-benzoïn. Iso-diphenyl-oxethylamine has been split up into optically active components, $[\alpha]_D = \pm 109{\cdot}6°$ (A. **307,** 79; B. **32,** 2377; **36,** 976). The quaternary ammonium bases obtained from the two dimethyl-oxethyl-amines by thorough methylation have the formula $C_6H_5CH(OH).CH(C_6H_5)N(CH_3)_3OH$, and are broken up by heating with water into trimethylamine, water, and **diphenyl-ethylene oxide** $C_6H_5CH.O.CHC_6H_5$, m.p. 69°, and **iso-diphenyl-ethylene oxide,** m.p. 42° (B. **48,** 884).

Diphenyl-ethylene-diamine, *stilbene-diamine* $C_6H_5CH(NH_2)CH(NH_2)C_6H_5$, melting at 91°, is produced by reducing benzile-dioxime with sodium and alcohol. It is resolved by crystallisation of its bitartrate into two optically active components (B. **28,** 3167).

The reduction of diphenyl-dinitro-ethanes and ethylenes with zinc dust and acetic acid produces **tetraphenyl-diethylene-diamine,** *tetraphenyl-piperazin* $NH[CH(C_6H_5).CH(C_6H_5)]NH$ (B. **34,** 627).

The *dieso-anhydride* of an **o, o-dioxy-hydro-benzoïn** $O.C_6H_4.\overline{CH.CH}.C_6H_4O$, has been obtained in two modifications, melting at 68° and 114°, by the reduction of salicyl-aldehyde with zinc dust and glacial acetic acid.

Benzoïn, *benzoyl-phenyl-carbinol* $C_6H_5.CH(OH).CO.C_6H_5$, melting at 134°, is produced when the hydro-benzoïns are oxidised with concentrated nitric acid, and by the condensation of two molecules of benzaldehyde with potassium cyanide in aqueous alcoholic solution.

This reaction is also shown by other aromatic aldehydes (see B. **25,** 293; **26,** 60; C. 1908, II. 1689). The products are ketone alcohols—*e.g. anisoïn* $CH_3O.C_6H_4CH(OH)CO.C_6H_4.OCH_3$; *cuminoïn*, etc., from anisic aldehyde, cuminol (see Furfurol, Phenyl-glyoxal)—and reduce Fehling's solution, being at the same time oxidised to the corresponding benziles.

d- and l-Benzoïn have been obtained by transformation of d- and l-mandelic acid amide with phenyl-magnesium bromide (C. 1909, II. 2005).

Chromic acid oxidises benzoïn to benzaldehyde and benzoic acid, while nitric acid changes it to benzile; nascent hydrogen reduces it to hydro-benzoïn. The latter and benzile are produced when benzoïn

is boiled with alcoholic potash. If air be simultaneously introduced, benzile is the chief product, and it is further changed to benzilic acid. By heating with concentrated alkali it is partly split up into benzyl alcohol and benzoic acid. Prolonged action also yields hydro-benzoïn, stilbene hydrate, etc. (B. **35,** 1982).

Benzoïn hydrazone melts at 75° (*J. pr. Ch.* 2, **52,** 124). *Semi-carbazone*, m.p. 206° (A. **339,** 257). The phenyl-hydrazones melt at 158° and 106° (B. **28,** R. 788); the α-oxime at 152°, the β-oxime at 99°; by oxidation with chromic acid the acetyl-β-benzoïn-oxime passes into the acetyl-γ-benzile-oxime, which determines its configuration (B. **38,** 69).

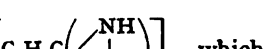
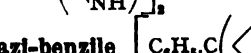
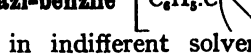
Alcohols and hydrochloric acid alkylise benzoïn: **methyl-benzoïn** $C_6H_5CH(OCH_3)COC_6H_5$ melts at 50°, and **ethyl-benzoïn** at 62° (B. **26,** 2412). **Iso-propyl-benzoïn,** m.p. 72°–75° (B. **26,** 2412; C. 1700, I. 454).

The HCl ester of benzoïn, **desyl-chloride** $C_6H_5CHClCOC_6H_5$, m.p. 68°, is formed by heating of benzoïn with thionyl chloride (B. **42,** 2348).

Desyl-bromide $C_6H_5.CHBrCOC_6H_5$, m.p. 55°, is obtained from desoxy-benzoïn (see below) and bromine. Aniline converts it into **desyl-anilide,** *benzoïn-anilide* $C_6H_5CH(NHC_6H_5)CO.C_6H_5$, m.p. 99°, which is also produced when aniline is heated together with benzoïn. When heated together with aniline hydrochloride to 160°, the product is **benzoïn-anile-anilide** $C_6H_5CH(NH.C_6H_5)C(NC_6H_5)C_6H_5$, m.p. 125°; and when with aniline and zinc chloride at still higher temperatures, **diphenyl-indol** (B. **26,** 1336, 2640).

Benzoïn-p-toluide $C_6H_5CH(NHC_6H_4.CH_3)CO.C_6H_5$, m.p. 145°, is formed in the condensation of benzaldehyde-toluidin by means of potassium cyanide (B. **29,** 1736). o-Diamines and benzoïn condense to *dihydro-quinoxalins*; urea and thio-ureas with benzoïn yield *glyoxalins*, while *oxazoles* are produced in the condensation of benzoïn with acid nitriles. For the condensation products of benzoïn with acetone and aceto-phenone, consult B. **26,** 65.

Benzile, dibenzoyl, *diphenyl-glyoxal* $C_6H_5.CO.CO.C_6H_5$, m.p. 90° and b.p. 347°, consists of beautiful yellow prisms. It is the most easily obtained α-diketone. It is produced on boiling stilbene bromide with water and silver oxide, and by digesting benzoïn with concentrated nitric acid.

Benzile and hydrazin hydrate form **hydra-benzile** and **bis-hydrazi-benzile**  , which yield **azi-benzile**  and **bis-azi-benzile**  on oxidation (B. **29,** 775). On heating in indifferent solvents the azi-benzile decomposes into nitrogen and diphenyl-ketene (B. **42,** 2346). **Benzile-mono-semi-carbazone,** m.p. 175°, heated with alcohol, splits off water and forms diphenyl-oxytriazin; **benzile-di-semi-carbazone,** m.p. 244° (A. **339,** 243).

Benzile-osazone $(C_6H_5)_2.C_2(NNH.C_6H_5)_2$, m.p. 225°, becomes triphenyl-oso-triazole on heating (A. **232**, 230; B. **26**, R. 198). An isomeric modification of benzile-osazone, m.p. 208°, has been obtained by the action of iodine and sodium ethylate upon benzal-phenyl-hydrazone. Derivatives have been similarly obtained. When heated above its melting-point it changes to the higher-melting modification (B. **29**, R. 863; **35**, 3519; A. **305**, 170; **324**, 310; C. 1909, I. 739).

One molecule of hydroxylamine, acting upon benzile, produces two isomeric *monoximes*, the α- melting at 134°, and the γ- at 113°. The former passes into the latter by heating it to 100° with alcohol, or upon dissolving it in glacial acetic acid with hydrochloric acid.

α-Monoxime and hydroxylamine form α-benzile-dioxime, while the γ-monoxime yields γ-benzile-dioxime (B. **22**, 540, 709). Compare B. **26**, 792, R. 52, for their behaviour with phenyl-hydrazin.

Both monoximes break down, upon heating, into benzo-nitrile and benzoic acid. The behaviour of the benzile-monoximes in the Beckmann oxime rearrangement is very interesting. It is effected by means of PCl_5: α-monoxime (1) yields benzoyl-benzimide chloride (2), readily decomposing into benzo-nitrile and benzoyl chloride, while the γ-monoxime (3) yields benzoyl-formic-acid, anilide chloride (4) (A. **296**, 279; B. **37**, 4295):

(1) $C_6H_5CCOC_6H_5$ (NOH) ⟶ (2) C_6H_5CCl (NCOC$_6H_5$); (3) $C_6H_5CCOC_6H_5$ (HON) ⟶ (4) $ClCCOC_6H_5$ (C_6H_5N)

In the first instance the hydroxyl exchanged positions with the phenyl residue, in the second with the benzoyl residue, which led to the above accepted configuration of the monoximes.

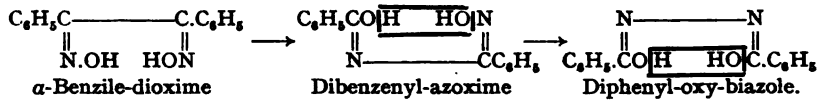
Two molecules of hydroxylamine convert benzile into two isomeric *benzile-dioximes*, the α- melting at 237°, and the β- at 207°. A third γ-benzile-dioxime has been prepared from γ-benzile-monoxime; it melts at 163°. The β-dioxime is the most stable; the other modifications rapidly change to it. Under certain conditions the γ-dioxime rearranges itself into the α-form (A. **274**, 33).

Three different esters are produced with acid anhydrides: *benzile-dioxime diacetates*—the α-form melting at 148°, the β- at 124°, and the γ- at 114°. Sodium hydroxide saponifies the α- and β-diacetates to their oximes, while the γ-acetate yields the *anhydride* $\begin{matrix} C_6H_5C:N \\ | \\ C_6H_5C:N \end{matrix}\!\!>\!O$, *diphenyl-furazane* (*q.v.*), which also results from all three dioximes by the exit of water. Potassium ferricyanide, in alkaline solution, oxidises all three to the *peroxide* $\begin{matrix} C_6H_5C=N-O \\ | \quad | \\ C_6H_5C=N-O \end{matrix}$, melting at 114°. This, when rapidly distilled, breaks down into two molecules of phenyl cyanate.

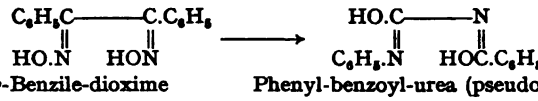
A complete picture is also afforded by the behaviour of the three dioximes in the Beckmann rearrangement, which has led to a formula for the present case of isomerism on the assumption that the oxime hydroxyls invariably exchange positions with the atomic groups adjacent to them (A. **274**, 1):

I. α-Benzile-dioxime yields chlorides with PCl_5 by a change in position first of the one and then of the second hydroxyl, which can be converted into the anhydrides: *dibenzenyl-azoxime* and *diphenyl-oxy-*

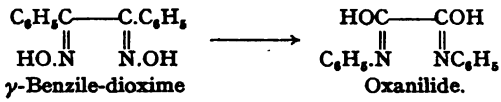
biazole (*q.v.*), whose hydrates are included in the following diagram for the sake of clearness :



II. γ-Benzile-dioxime in the first stage of the reaction also yields dibenzenyl-azoxime, but by a second change in position *phenyl-benzoyl-urea* is produced :



III. β-Dioxime by a double change in position yields *oxanilide* :



The ready transition of the γ-diacetate into furazane is not in harmony with the preceding configuration of the dioximes ; this might rather be expected from the α-diacetate.

The analogy of the benzile-dioximes with the osazones of dioxo-succinic ester is rather remarkable (I. 528). These osazones also occur in three forms, one of which is stable and the other two unstable, so that the assumption of similar causes for the isomerism is not yet excluded (B. **28,** 64).

Aniline and benzile heated to 200° yield *benzile-monanile* $C_6H_5CO.C(NC_6H_5)C_6H_5$, melting at 106° ; on adding P_2O_5 the product is *benzile-dianile* $C_6H_5C(NC_6H_5)C(NC_6H_5)C_6H_5$, melting at 142° (B. **25,** 2600 ; **26,** R. 700). Benzile, being an o-diketone, is particularly well adapted for the formation of heterocyclic rings. It condenses with ethylene-diamine to a *dihydro-pyrazine* derivative, with ortho-diamines to *quinoxalins*, with o-amido-diphenylamine to a *stilbazonium base* (see this), with ureas and thio-ureas to *ureïns* and *diureïns*, with semi-carbazide to *oxy-diphenyl-triazine*, etc. Hydriodic acid reduces it to desoxy-benzoïn, while chromic acid oxidises it to benzoic acid. On standing with potassium cyanide and alcohol it breaks down into benzoic acid and benzaldehyde. See B. **28,** R. 465 ; **29,** R. 645, 865 ; C. 1897, I. 596 ; 1903, I. 877 ; 1905, II. 243, for the condensation of benzile with malonic ester and aceto-acetic ester.

The conversion of benzile into benzilic acid by fusion with caustic potash or upon boiling with alcoholic potash is important :

$$C_6H_5COCOC_6H_5 \xrightarrow{H_2O} (C_6H_5)_2C(OH)COOH.$$

Phosphorus pentachloride changes benzile to **chloro-benzile** $C_6H_5.COCCl_2C_6H_5$, m.p. 61°, and, later, to **tolane tetrachloride** $C_6H_5CCl_2CCl_2C_6H_5$, m.p. 163°. The latter has also been obtained synthetically on heating benzo-trichloride with copper, whereas benzile is produced when it is heated together with glacial acetic acid or sulphuric acid.

As benzile is obtained from benzoïn, so **anisile** $(CH_3O.C_6H_4CO)_2$,

melting at 133°, **cuminile** $(C_3H_7.C_6H_4CO)_2$, melting at 84°, have been prepared by the action of nitric acid upon anisoïn and cuminoïn. Anisile and a **hexamethoxy-benzile** $[(CH_3.O)_3C_6H_2CO]_2$, m.p. 189°, have been obtained by alkaline reducing agents from anisamide and trimethyl-gallamide (B. **24,** R. 523).

These benziles, when fused with caustic potash, yield :

Anisilic acid, cumilic acid, and *hexamethoxy-benzilic acid* (see above).

The *osazones* of several substituted benziles, like *salicile, cuminile, anisile, piperile,* like benzile-osazone itself, have been obtained by the action of atmospheric oxygen upon the alkaline alcoholic solutions of the phenyl-hydrazones of the corresponding aldehydes : salicyl-aldehyde, piperonal, etc. (A. **308,** 1).

p_2-Tetramethyl-diamido-benzile $(CH_3)_2NC_6H_4.CO.COC_6H_4N(CH_3)_2$, m.p. 198°, is obtained by heating oxalyl chloride with excess of dimethyl-aniline (B. **42,** 3487).

ALCOHOL DERIVATIVES OF STILBENE are not known in a free condition ; when their esters are saponified, isomeric ketones are obtained for the most part (see Phenyl-vinyl alcohols) :

Bromo-stilbene	$C_6H_5CBr:CHC_6H_5$	$\xrightarrow{H_2O}$ $C_6H_5CO.CH_2C_6H_5$	Desoxy-benzoïn
Iso-benzile	$C_6H_5C(OCOC_6H_5):C(OCOC_6H_5)C_6H_5$	$\rightarrow C_6H_5CO.CH(OH)C_6H_5$	Benzoïn.

However, benzoïn reacts in most cases as if it were an unsaturated glycol with the formula $C_6H_5C(OH):C(OH)C_6H_5$.

Monochloro-stilbene $C_6H_5CH:CCl.C_6H_5$ is an oil boiling at 320°–324°. It is produced when PCl_5 acts upon desoxy-benzoïn, and by the action of alcoholic potash on stilbene dichloride. When boiled with glacial acetic acid it is transformed into an isomeric modification, melting at 54°. Chlorine and bromine convert it into **chloro-stilbene dichloride** $C_6H_5CCl_2.CHCl.C_6H_5$, m.p. 103°, and **chloro-stilbene dibromide,** m.p. 127° (C. 1897, I. 858). **Methyl-chloro-stilbene** $C_6H_5C(CH_3):CClC_6H_5$ is obtained from methyl-desoxy-benzoïn, and behaves similarly. It is an oil, and melts at 118° (B. **25,** 2237 ; **29,** R. 34). **Monobromo-stilbene,** m.p. 31°, results on treating β-stilbene dibromide, m.p. 110°, with alcoholic potash ; whereas the stilbene dibromide, m.p. 237°, yields an iso-bromo-stilbene, m.p. 19°. On the application of heat the latter passes into the solid isomeride. Reduction with zinc and alcohol converts iso-bromo-stilbene into liquid iso-stilbene.

Diacetyl-dioxy-stilbene, *stilbene-glycol diacetate* $C_6H_5C(OCOCH_3):C(OCOCH_3)C_6H_5$, α-modification, m.p. 153°, β-modification, m.p. 110°, is formed by the reduction of benzile in acetic anhydride and sulphuric acid with zinc dust (A. **306,** 142).

Iso-benzile, *stilbene-glycol dibenzoate* $C_6H_5C(O.COC_6H_5):C(OCOC_6H_5)C_6H_5$, colourless needles, m.p. 156°, is obtained by the action of metallic sodium upon the ethereal solution of benzoyl chloride (Vol. I.). It is a polymeride of benzile. When saponified with caustic potash it is resolved into benzoic acid and benzoïn (B. **24,** 1264).

Dichloro-stilbene, *tolane dichloride* $C_6H_5CCl:CCl.C_6H_5$, exists in two modifications : α-, m.p. 143° ; β-, m.p. 63°. Both are formed by the addition of chlorine to tolane, or by the reduction of tolane tetrachloride with iron and acetic acid, as well as from chloro-stilbene

dichloride (see above) with caustic potash. **Chloro-bromo-stilbene** $C_6H_5CCl : CBrC_6H_5$, m.p. 174°, is similarly prepared from chloro-stilbene dibromide. **Dibromo-stilbenes,** *α*- melting at 208°, and *β*- melting at 64°, are obtained from tolane and bromine. Concerning p_2-dioxy-derivatives of dichloro-stilbene, and their conversion into the methylene-quinones of the dibenzyl series, see *J. pr. Ch.* 2, **59,** 228; A. **325,** 67.

CARBOXYLIC ACIDS OF THE DIBENZYL GROUP.—These consist of: (*a*) those in which the carboxyl group is in the benzene nucleus; (*b*) such as have the carboxyl group in the side chain: diphenylated fatty acids.

The first group is composed chiefly of a series of o-carboxylic acids produced by phthalic anhydride condensations:

Dibenzyl-o, o'- and -p, p'-dicarboxylic acid $CO_2HC_6H_4CH_2.CH_2C_6H_4CO_2H$, m.p. 231° and over 320°, are formed by the oxidation of o- and p-toluic acid with potassium persulphate (B. **37,** 3215).

o-Desoxy-benzoïn-carboxylic acid $C_6H_5.CH_2.CO.C_6H_4.COOH(+H_2O)$, melting at 75°, is formed when boiling alkalies act on the corresponding lactone. **Benzylidene-phthalide,** *benzal-phthalide* $C_6H_4.CH : \overline{CC_6H_4CO}\overline{O}$, melting at 99°, which results from the condensation of phthalic anhydride and phenyl-acetic acid with the elimination of CO_2.

By means of nitro-benzal-phthalide, benzal-phthalide can be changed to **iso-benzal-phthalide** $C_6H_5\overline{C : CH.C_6H_4.CO}\overline{O}$, melting at 91°, the anhydride of *β*, **o-desoxy-benzoïn-carboxylic acid** $C_6H_5.CO.CH_2.C_6H_4.CO_2H$, melting at 163°. The latter is made by decomposing *β*-phenyl-hydrindone with caustic soda, and from homo-phthalic anhydride with benzene and $AlCl_3$ (B. **31,** 377). Benzal-phthalide sustains a different rearrangement under the influence of sodium alcoholate; the sodium salt of *β*-phenyl-diketo-hydrindene is then produced:

$$C_6H_5.\overline{C : CH.C_6H_4.CO}\overline{O} \longleftarrow C_6H_5CH : \overline{C.C_6H_4.CO}\overline{O} \longrightarrow C_6H_4\overline{CH.CO.C_6H_4.CO}\overline{O}$$

Iso-benzal-phthalide — Benzal-phthalide — Phenyl-diketo-hydrindene.

Hydrazin converts benzal-phthalide into **benzyl-phthalazone** $C_6H_5.CH_2.\overset{\|}{C}\overset{N\text{——}NH}{\underset{}{}}\overset{|}{C}.C_6H_4.CO$. By reduction with glacial acetic acid and zinc it passes into **benzyl-phthalimidine** $C_6H_5CH_2.\overline{CHC_6H_4.CO.NH}$, melting at 137°. It can also be obtained by the reduction of benzal-phthalimidine (B. **29,** 1434, 2743). Homologues of benzal-phthalide, see B. **32,** 1104, etc.

o, o-Desoxy-benzoïn-dicarboxylic acid $COOH.C_6H_4.CH_2.CO.C_6H_4.COOH$, melting at 239°, is obtained upon heating monophthalic acid and sodium acetate (B. **24,** 2820). The reduction of desoxy-benzoïn-mono- and dicarboxylic acids yields **dibenzyl-mono-** and **dicarboxylic acids,** melting at 131° and 225°. The oxidation of o-desoxy-benzoïn-carboxylic acid produces **o-benzile-carboxylic acid** $C_6H_5.CO.CO.C_6H_4.COOH$, occurring in two modifications, one *yellow* in colour, melting at 141°, and another *white,* melting at 125°–130° (B. **28,** 1344, 2079; **29,** 2745; C. 1898, II. 481).

o, o-Benzile-dicarboxylic acid, *diphthalylic acid* $(COOHC_6H_4CO)_2$ or

$\overline{OCOC_6H_4}C(OH).\overline{C(OH)C_6H_4COO}$, m.p. 273°, gives with acetyl chloride a diacetyl derivative; the acid esters are colourless, like the acid itself, while the neutral esters are yellow. Diphthalide acid is formed by the oxidation of chryso-quinone and chryso-ketone (A. **311**, 264). The acid is formed from phthalic anhydride with zinc dust and acetic acid and subsequent oxidation, or by the oxidation of **diphthalyl** $\overline{O.OC.C_6H_4}C : \overline{CC_6H_4COO}$, melting at 334°. This latter body has been produced by the condensation of phthalide and phthalic anhydride with potassium cyanide (see formation of benzoïn, p. 615). **Tetramethoxy-diphthalyl** $\overline{O.OC.C_6H_2(OCH_3)_2}C : \overline{CC_6H_2(OCH_3)COO}$ (B. **24**, R. 820; cp. B. **26**, 540) is similarly made by the condensation of opianic ester.

Tetramethoxy-diphthalyl $\overline{OOCC_6H_2(OCH_3)_2}C : \overline{CC_6H_2(OCH_3)_2COO}$ (B. **24**, R. 820; **26**, 540).

Dithio-diphthalyl $\overline{SCO.C_6H_4}C : \overline{CC_6H_4COS}$, yellow-green needles, m.p. 333°, see B. **31**, 2646.

Dihydro-diphthalyl-di-imide $\overline{NH.CO.C_6H_4}.CH.\overline{CHC_6H_4CO.NH}$, melting with decomposition at 284°, results from the condensation of two molecules of phthalic anhydride with methyl-alcoholic ammonia. This substance is isomeric with indigo white (cp. B. **29**, 2745).

Hydro-diphthalyl-lactonic acid $HOOCC_6H_4CH_2.\overline{CHC_6H_4COO}$, m.p. 198°, is formed on heating homo-phthalic acid to 230° (B. **31**, 376).

Dibenzyl-carboxylic acid *α-phenyl-hydro-cinnamic acid, α, β-diphenyl-propionic acid, benzyl-phenyl-acetic acid* $C_6H_5CH_2CH(C_6H_5)COOH$, appears in three physical isomerides, melting at 95°, 89°, 82°, boiling at 335° (B. **25**, 2017). Its *nitrile* results upon introducing benzyl into benzyl cyanide. **α-Phenyl-o-amido-hydro-cinnamic acid,** melting at 148°, is obtained in the reduction of α-phenyl-o-nitro-cinnamic acid (B. **28**, R. 391). It changes very readily into its lactame—*β-phenyl-hydrocarbo-styrile* $C_6H_4\begin{cases}CH_2—CH(C_6H_5)CO\\ NH\end{cases}$, melting at 174°.

αβ-Diphenyl-valeric acid $C_2H_5CH(C_6H_5)CH(C_6H_5)COOH$, m.p. 178°; its nitrile, m.p. 115°, is formed by attaching C_2H_5MgI to α-phenyl-cinnamic acid nitrile (C. 1906, II. 46).

Stilbene-carboxylic acid, *α-phenyl-cinnamic acid* $C_6H_5CH : C(C_6H_5)CO_2H$, melting at 172°, is formed in the condensation of benzaldehyde with phenyl-acetic acid. Allo-phenyl-cinnamic acid, m.p. 137° (C. 1897, II. 663) is also formed; also stilbene on heating and expulsion of CO_2 (*J. pr. Ch.* 2, **61**, 1). **α-Phenyl-cinnamic nitrile,** m.p. 86°, from benzyl cyanide, benzaldehyde, and sodium ethylate. By reduction it becomes α-phenyl-hydro-cinnamic acid, but does not add bromine. The action of bromine upon the sodium salt produces bromo-stilbene (B. **26**, 659). **α-Phenyl-o-amido-cinnamic acid,** m.p. 186°, the reduction product of o-nitro-α-phenyl-cinnamic acid, obtained in the condensation of o-nitro-benzaldehyde with phenyl-acetic acid, yields β-phenanthrene-carboxylic acid (*q.v.*) (B. **29**, 496) when its diazo-derivative is shaken with copper in powder form. The nitrile of phenyl-o-amido-cinnamic

acid is easily transposed into **α-amido-β-phenyl-quinolin,** so that synthesis gives the latter instead of the nitrile (B. **32,** 3399). The lactone of phenyl-o-oxy-cinnamic acid, **α-phenyl-cumarin** $C_6H_4\begin{cases}[1]CH:CC_6H_5\\[2]O\text{——}CO\end{cases}$, m.p. 140°, is formed from salicyl-aldehyde and phenyl-acetic acid (*J. pr. Ch.* 2, **61,** 178). **o-, m-,** and **p-Oxy-benzal-benzyl cyanide** $HOC_6H_4CH:C(CN)C_6H_5$, m.p. 104°, 107°, and 192° (B. **37,** 3163).

α-Stilbene-methyl-ketone, 3, 4-*diphenyl-butenone-2* $C_6H_5CH:C(C_6H_5)COCH_3$, m.p. 51°, from benzaldehyde and phenyl-acetone with gaseous HCl. It does not add bromine, but gives on reduction with sodium amalgam **3, 4-diphenyl-butanone** $C_6H_5CH_2.CH(C_6H_5)COCH_3$, b.p. 310° (M. **22,** 659).

Stilbene-propionic acid, *γ, δ-diphenyl-allyl-acetic acid* $C_6H_5CH:C(C_6H_5).CH_2.CH_2COOH$, m.p. 106°, from sodium-α-phenyl-glutarate with benzaldehyde and acetic anhydride (B. **34,** 4177).

Desyl-acetic acid, *ββ-phenyl-benzoyl-propionic acid* $C_6H_5.COCH(C_6H_5).CH_2.COOH$, m.p. 161°, is obtained as ester from the interaction of sodium desoxy-benzoïn and bromacetic ester (A. **319,** 164); it is also formed from phenyl-succinic-β-methyl ester acid chloride with benzene and $AlCl_3$. By treatment with acetic anhydride sulphuric acid in the cold the acid gives unstable **diphenyl-Δ^2-croto-lactone** $C_6H_5\overline{C:C(C_6H_5)CH_2CO}O$, m.p. 100°, which, on boiling with acetic anhydride or treatment with alkalies, passes into the stable **diphenyl-Δ^1-croto-lactone** $C_6H_5\overline{CH.C(C_6H_5):CHCO}O$, m.p. 152°. Both lactones, treated with alkalies, regenerate desyl-acetic acid; by the action of permanganate or bromine the stable diphenyl-croto-lactone gives **desylene-acetic acid** $C_6H_5CO.C(C_6H_5):CHCOOH$, m.p. 139°, which has also been obtained from desylene-malonic ester, the condensation product of benzile with malonic ester (A. **319,** 155). Desyl-acetic acid and the stable diphenyl-croto-lactone are also formed from **diphenyl-α-keto-butyro-lactone** (1), the condensation product of phenyl-pyro-racemic acid and benzaldehyde, which, on reduction, first yields an oxy-lactone (2), and from the latter, by rejection of water, diphenyl-croto-lactone (3) (B. **31,** 2218; **36,** 2344; A. **333,** 160).

$$\overset{(1)}{C_6H_5CH.CH(C_6H_5)}\!\!\begin{array}{l}\diagdown\\ O\text{——}CO\end{array}\!\!\diagup CO \rightarrow \overset{(2)}{C_6H_5CH.CH(C_6H_5)}\!\!\begin{array}{l}\diagdown\\ O\text{——}CO\end{array}\!\!\diagup CHOH \rightarrow \overset{(3)}{C_6H_5CH.C(C_6H_5)}\!\!\begin{array}{l}\diagdown\\ O\text{——}CO\end{array}\!\!\diagup CH.$$

Dibenzyl-dicarboxylic acid, sym. diphenyl-succinic acid $\begin{matrix}C_6H_5.CH.COOH\\ |\\ C_6H_5.CH.COOH\end{matrix}$, occurs similarly to the dialkyl-succinic acids in two isomeric forms. The *α-acid* ($+H_2O$) is produced on heating phenyl-bromacetic acid (2 mols.) with alcoholic CNK, also (together with the β-acid, m.p. 229°) from stilbene-dicarboxylic acid with sodium amalgam. The acid, containing one molecule of water, melts at 185° when rapidly heated; it loses water and remelts at 220°. When heated to 200° with hydrochloric acid it changes to the β-acid. Its *anhydride,* melting at 116°, is readily produced by means of acetyl chloride.

The β-acid yields an *anhydride* (but with more difficulty) when heated with acetyl chloride (B. **23,** 117, R. 574; A. **259,** 61). It melts at 112°.

The *nitriles* $C_6H_5CH(CN)CH(CN)C_6H_5$, the α- melting at 160° and

the β- melting at 240°, result from the condensation of phenyl-aceto-nitrile with mandelo-nitrile by means of potassium cyanide (B. **25,** 289 ; **26,** 60). Both nitriles yield the β-acid when they are saponified.

α, β-**Diphenyl-glutaric acid** $C_6H_5CH(CO_2H)CH(C_6H_5)CH_2CO_2H$, m.p. 231° ; its ester is obtained by attaching phenyl-acetic ester to cinnamic acid ester by means of sodium ethylate (B. **42,** 4497 ; C. 1908, I. 1776).

β, γ-**Diphenyl-adipic acid** $CO_2HCH_2CH(C_6H_5)CH(C_6H_5)CH_2CO_2H$, two modifications, m.p. 270° and 170°. Dimethyl esters, m.p. 175° and 73°, are formed by the reduction of cinnamic acid ester with Al amalgam, together with hydro-cinnamic acid ester. The great similarity to truxillic acid is noteworthy (A. **348,** 16 ; B. **39,** 4089).

Stilbene-dicarboxylic acid, diphenyl-maleic acid, decomposes immediately when separated from its salts, like the dialkylic maleïc acids, into water and its *anhydride* $\begin{matrix} C_6H_5.C.CO \\ \| \\ C_6H_5.C.CO \end{matrix}\!\!>\!O$, m.p. 155°. The latter condenses, like phthalic anhydride, with phenyl-acetic acid and quickly changes to **benzal-diphenyl-maleïde** $\begin{matrix} C_6H_5C{-}C{=}CH.C_6H_5 \\ \| \\ C_6H_5C{-}CO \end{matrix}\!\!>\!O$, which behaves just like benzal-phthalide (B. **24,** 3854). The salts of diphenyl-maleïc acid are formed when **dicyano-stilbene** $C_6H_5C(CN) : C(CN)C_6H_5$, m.p. 158°, are saponified with alcoholic potash. This nitrile is produced when phenyl-chloraceto-nitrile is treated with CNK or $NaOC_2H_5$, or by the action of sodium alcoholate and iodine upon phenyl-aceto-nitrile (B. **25,** 285, 1680).

Stilbene-succinic acid, *γ-benzylidene-γ-phenyl-pyro-tartaric acid,* from benzoïn with succinic ester and sodium alcoholate. With Br the acid gives a bromo-lactonic acid, which on heating yields an unsaturated lactonic acid $C_6H_5\overline{CH.C(C_6H_5) : C(COO)}CH_2COOH$ and a dilactone $C_6H_5\overline{CH.C(C_6H_5).CH(COO)}CH_2COO$ (A. **308,** 156).

4, 5-Diphenyl-octane-2, 7-dione, *αβ-diacetonyl-dibenzyl* $\begin{matrix} C_6H_5.CH.CH_2.CO.CH_3 \\ | \\ C_6H_5.CH.CH_2.CO.CH_3 \end{matrix}$, m.p. 161° and b.p. 335°–340°, may be regarded as a derivative of dibenzyl. It might be designated **αβ-diacetonyl-dibenzyl** It results in the reduction of two molecules of benzylidene-acetone in feebly acid or neutral solution (B. **29,** 380, 2121). Homologous diketones are formed from homologous benzylidene-ketones by reduction (B. **35,** 966).

C. *Tri-, Tetra-, Penta-, and Hexaphenyl-ethane Group.*—**Triphenyl-ethane** $(C_6H_5)_2CHCH_2C_6H_5$, b.p. 348° (B. **37,** 1455), by reduction of **triphenyl-ethylene,** α-phenyl-stilbene $(C_6H_5)_2C : CHC_6H_5$, m.p. 68°, b.p. 221° ; also by extracting water from benzyl-diphenyl-carbinol (B. **37,** 1429, 1455).

Triphenyl-ethanone, or *triphenyl-vinyl alcohol* $(C_6H_5)_2.CH.CO.C_6H_5$ or $(C_6H_5)_2.C : C(OH)C_6H_5$, m.p. 136°, results from the action of benzene and aluminium chloride upon chloral, upon dichloro- or trichoro-acetyl chloride (B. **29,** R. 292 ; A. **296,** 219 ; **368,** 92) ; also from **triphenyl-ethylene-glycol** $(C_6H_5)_2C(OH)CH(OH)C_6H_5$, m.p. 164°, the product of the action of C_6H_5MgBr upon benzoïn or mandelic ester (B. **37,** 2762),

on heating with 25 per cent. H_2SO_4 (C. 1908, I. 830). Potassium permanganate oxidises it to benzo-phenone and benzoic acid, while alcoholic potash resolves it into diphenyl-methane and benzoic acid. With hydroxylamine chlorohydrate it yields an oxime, m.p. 182° (C. 1906, II. 1061). With acetyl chloride and benzoyl chloride we obtain triphenyl-vinyl acetate and benzoate derivatives of the alcohol form.

Bromine in carbon disulphide converts it into **triphenyl-brom-ethanone** $(C_6H_5)_2CBrCOC_6H_5$, m.p. 97°, in glacial acetic acid; however, by replacement of bromine with hydroxyl **triphenyl-oxy-ethanone,** *phenyl-benzoïn* $(C_6H_5)_2C(OH)COC_6H_5$, m.p. 84°, results. This is also obtained by the oxidation of diphenyl-ethanone with HNO_2, and from benzile with C_6H_5MgBr (B. **32,** 650; **37,** 2758). Reduction of triphenyl-ethanone or its bromination product gives **triphenyl-ethanol,** *benzo-hydryl-, phenyl-, carbinol* $(C_6H_5)_2CH.CH(OH)C_6H_5$, m.p. 87°, isomeric with benzyl-, diphenyl-carbinol (see above) (C. 1897, II. 661).

Triphenyl-methyl-ethane, *α, α, β-triphenyl-propane* $(C_6H_5)_2CH.CH(CH_3)C_6H_5$, is probably the product obtained by the reduction of diphenyl-indone with phosphorus and hydriodic acid. Diphenyl-indone is an intermediate product in the condensation of benzo-phenone chloride with phenyl-acetic ester, whereby there results—

Triphenyl-acrylic ester $(C_6H_5)_2C : C(C_6H_5)COOR$. The acid, melting at 213°, corresponding to this ester is obtained from its *nitrile,* melting at 163°, the condensation product of benzo-phenone chloride and benzyl cyanide (B. **28,** 1784; **29,** 2841) The acid is also obtained from **triphenyl-propionic acid** $(C_6H_5)_2CH.CH(C_6H_5)CO_2H$, m.p. 211°, the product of attachment of C_6H_5MgBr to α-phenyl-cinnamic ester, by bromination and rejection of HBr (C. 1905, I. 824; B. **34,** 1963). When diphenyl-indone is fused with caustic potash it yields an acid, melting at 186°, which is isomeric with triphenyl-acrylic acid. It is probably—

α, **β-Diphenyl-vinyl-o-benzoic acid** $COOH[2]C_6H_4C(C_6H_5) : CH.C_6H_5$. Both acids, when heated with $ZnCl_2$, revert again to diphenyl-indone (B. **30,** 1282).

Tetra-phenyl-ethane $(C_6H_5)_2CH.CH(C_6H_5)_2$, melting at 209° and boiling at 370°–383°, is formed when benzo-phenone or benzo-hydrol chloride $(C_6H_5)_2CHCl$ is heated with zinc, and thio-benzo-phenone with copper; further, by the reduction of tetraphenyl-ethylene with sodium and alcohol, of benzo-pinacone or benzo-pinacolin (see below) with hydriodic acid and phosphorus, as well as by the condensation of stilbene bromide, of tetrabromo-ethane, or of chloral with benzene and $AlCl_3$ (B. **18,** 657; **26,** 1952; A. **296,** 221).

Unsym. tetraphenyl-ethane $(C_6H_5)_3C.CH_2C_6H_5$, m.p. 144°, is formed by the action of $C_6H_5CH_2MgCl$ upon triphenyl-chloro-methane, or of $(C_6H_5)_3CMgCl$ or $(C_6H_5)_3CK$ upon benzyl chloride (B. **41,** 435).

Tetraphenyl-ethylene $(C_6H_5)_2C : C(C_6H_5)_2$, melting at 221°, is formed, together with tetraphenyl-ethane, from benzo-phenone, and is also obtained on heating benzo-phenone chloride with silver or with zinc dust, together with the benzo-pinacolins (B. **29,** 1789), also by heating benzo-phenone chloride with diphenyl-methane (B. **43,** 2958). By oxidation it is split up into two molecules of benzo-phenone. It unites with chlorine in CCl_4 solution to form **tetraphenyl-ethylene dichloride** $(C_6H_5)_2CCl.CCl.(C_6H_5)_2$, m.p. 186°, which is also obtained

from benzo-phenone chloride by the action of molecular silver or mercury as well as sodium iodide in acetone solution. With two molecules of $CHCl_3$ or CCl_4 it gives crystalline addition products. Two chlorine atoms in the tetraphenyl-ethylene dichloride are very loosely bound. On heating alone it splits up into tetraphenyl-ethylene and chlorine, the latter partly acting as a substituent. Upon boiling with water we obtain α-benzo-pinacolin; with methyl alcohol, β-benzo-pinacolin. The action of $AlCl_3$ upon the benzene solution brings about rejection of 2HCl and formation of 9, 10-diphenyl-phenanthrene (B. **43,** 1533, 2940).

Tetra-methyl-diamido-tetraphenyl-ethylene $(CH_3)_2NC_6H_4(C_6H_5)C : C(C_6H_5)C_6H_4N(CH_3)_2$, m.p. 225°, by reduction of dimethyl-amido-benzo-phenone with tin and HCl. In acid solution with oxidising agents like $FeCl_3$ it gives intensely red colorations (B. **39,** 3765).

The *alcohols* of the tetraphenyl group are the pinacones of benzo-phenone and its homologues. They are formed, like the pinacones of the aliphatic series, from the ketones, together with secondary alcohols, by the action of nascent hydrogen.

Benzo-pinacone, *tetraphenyl-ethylene-glycol* $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$, melts at 185° and splits into benzo-phenone and benzo-hydrol. It sustains a like change when boiled with alcoholic potash. It is formed from benzo-phenone by the action of zinc and sulphuric acid or by the decomposition of sodium benzo-phenone (B. **25,** R. 15), or by condensation of oxalic methyl ester, or benzilic acid ester, with C_6H_5MgBr (C. 1903, I. 967; B. **37,** 2761). By heating with concentrated HCl or dilute sulphuric acid to 200°, benzo-pinacone, like the ordinary pinacone (Vol. I.), passes with rejection of water and migration of a phenyl group into the so-called **β-benzo-pinacolin** $(C_6H_5)_3C.COC_6H_5$, m.p. 170°, which is also obtained synthetically by the action of triphenyl-methyl-magnesium chloride upon benzaldehyde and subsequent oxidation, as well as from triphenyl-acetyl chloride and phenyl-magnesium bromide (B. **43,** 1140); its constitution is proved not only by these syntheses, but also by the splitting up into triphenyl-methane and benzoic acid on heating with soda lime and by the formation of triphenyl-carbinol and benzoic acid during oxidation. β-Benzo-pinacolin can also be obtained direct from benzo-phenone with zinc dust and acetyl chloride besides the isomeric **α-benzo-pinacolin,** m.p. 203°, which is easily converted by acids into β-benzo-pinacolin and is probably *tetraphenyl-ethylene oxide* $(C_6H_5)_2C.O.C(C_6H_5)_2$ (B. **29,** 2158; **43,** 1153). By heating with zinc ethyl β-benzo-pinacolin can be reduced to **benzo-pinacolin alcohol** $(C_6H_5)_3C.CH(OH)C_6H_5$, m.p. 151°, which on heating with acetic anhydride passes into tetraphenyl-ethylene with return of the phenyl group (B. **23,** R. 769) (cp. the analogous formation of tetramethyl-ethylene from pinacolin alcohol, Vol. I.). p_4-Tetrachloro-benzo-pinacolin, see C. 1907, I. 475.

Pentaphenyl-ethane $(C_6H_5)_3C.CH(C_6H_5)_2$, m.p. 179°, in CO_2 atmosphere, is formed by the transposition of diphenyl-methyl-magnesium bromide $(C_6H_5)_2CH.MgBr$ with triphenyl-chloro-methane (B. **39,** 1466), as well as the action of zinc upon a mixture of diphenyl-bromo-methane and triphenyl-chloro-methane in acetic ester (B. **43,** 2945). It is not so stable as the entirely stable tetraphenyl-ethane, and in that respect approaches the easily dissociated hexaphenyl-ethanes. On

heating in the air it is decomposed with absorption of oxygen. By boiling its solutions in anisol or benzoic acid ester it is split up into triphenyl-methyl-, or hexaphenyl-ethane and sym. tetraphenyl-ethane (B. **48**, 3541).

$$2(C_6H_5)_3C{-}CH(C_6H_5)_2 \longrightarrow [(C_6H_5)_3C{-}]_2{+}[{-}CH(C_6H_5)_2]_2.$$

Similarly, it decomposes on heating with benzene and HCl, or by the action of sulphuryl chloride (B. **40**, 367; **43**, 2945).

Pentaphenyl-ethyl alcohol $(C_6H_5)_3C.C(OH)(C_6H_5)_2$, m.p. 179°, from β-benzo-pinacolin and C_6H_5MgBr (B. **43**, 1145).

Hexaphenyl-ethane, m.p. about 95°: this exceedingly interesting hydrocarbon was first obtained by Gomberg (1900, B. **33**, 3150) by the action of zinc upon benzene solution of triphenyl-chloro-methane (see A. **372**, 17). It is distinguished by its great reactivity, which makes it appear as an unsaturated compound. In solution it greedily absorbs atmospheric oxygen with the formation of a *peroxide* $[(C_6H_5)_3C]_2O_2$, m.p. 185°, which on treatment with concentrated sulphuric acid gives triphenyl-carbinol. Iodine solution is also instantly decolourised with formation of triphenyl-iodo-methane (B. **35**, 1824). With benzene, ether, acetic ester, etc., hexaphenyl-ethane forms crystal compounds which are easily dissociated (B. **38**, 1333, 2447). Colourless in the solid state, hexaphenyl-ethane has a yellow colour when dissolved. This colour, on shaking with air, disappears with a precipitation of the peroxide mentioned, but the colour reappears in a short time. The substance therefore exists in solution in a colourless and a yellow modification, in a state of equilibrium dependent upon the solvent and the temperature. Only the coloured modification shows characteristic unsaturated behaviour of hexaphenyl-ethane (Schmidlin, B. **41**, 2471). It is assumed that by the binding of the six unsaturated phenyl groups the affinities of the ethane-carbon atoms are so much engaged that the affinities required for binding these two carbon atoms do not suffice for a solid and normal binding, and that therefore the hexaphenyl-ethane passes in solution partly into the yellow unsaturated, and therefore very reactive free radicle, **triphenyl-methyl**:

$$(C_6H_5)_3C{-}C(C_6H_5)_3 \rightleftarrows 2(C_6H_5)_3C{-}.$$

Triphenyl-methyl is therefore the first example of a compound in which one carbon atom only binds three univalent atomic groups, and in which, therefore, carbon appears as a trivalent element. Hexaphenyl-ethane therefore shows a behaviour parallel with that of nitrogen tetroxide, which, while colourless at low temperatures, decomposes on heating into the coloured and very reactive hemimeric nitrogen dioxide. From this point of view it is remarkable that the organic radicle $(C_6H_5)_3C$ unites with the inorganic radicles NO and NO_2 to form a colourless **triphenyl-nitroso-methane** $(C_6H_5)_3C.NO$ and **triphenyl-nitro-methane** $(C_6H_5)_3C.NO_2$, m.p. 147°, which, on heating, easily decompose into their components (B. **44**, 1169).

The action of concentrated HCl converts hexaphenyl-ethane and triphenyl-methyl into **p-diphenyl-methyl-tetraphenyl-methane** $(C_6H_5)_2CHC_6H_4C(C_6H_5)_3$ (B. **37**, 4790).

Besides the methods indicated, the following have also been used for preparing hexaphenyl-ethane: (1) from triphenyl-methyl-magnesium chloride and triphenyl-chloro-methane (B. **41,** 423); (2) by electrolysis of triphenyl-bromo-methane in SO_2 solution (A. **372,** 11); (3) from hydrazo-triphenyl-methane $(C_6H_5)_3C.NH.NH.C(C_6H_5)_3$ by oxidation with potassium hypo-bromite by way of the unstable azo-compound (B. **42,** 3020).

While solid hexaphenyl-ethane does not pass into triphenyl-methyl, and even its solution does so only in small quantities (see B. **37,** 2041; **42,** 3028), the **tribiphenyl-methyl** $(C_6H_5.C_6H_4)_3C$, obtained by withdrawal of halogen from tribiphenyl-chloro-methane by means of powdered copper, which is dark violet even in the solid condition, only exists in solution in the form of the free radicle, as indicated by the molecular weight. In contrast with these, a hydrocarbon obtained from the similarly built **biphenylene-biphenyl-chloro-methane** $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!CCl(C_6H_4C_6H_5)$ is colourless even in solution and incapable of uniting with oxygen or halogen. It must therefore be regarded as undissociated **dibiphenylene-dibiphenyl-ethane** $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!C\!-\!\!-\!\!-\!\!-\!C\!<\!\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$. Between these two extremes the similarly obtained hydrocarbons, diphenylene-diphenyl-ethane, tetraphenyl-dibiphenyl-ethane, and diphenyl-tetrabiphenyl-ethane occupy a middle position, decomposing in solution with more or less ease into the hemimeric triaryl-methyls (Schlenk, A. **372,** 1; B. **43,** 1753).

Tetraphenyl-ethane-dicarboxylic acid, tetraphenyl-succinic acid $\begin{matrix}(C_6H_5)_2C.COOH\\(C_6H_5)_2C.COOH\end{matrix}$, melting at 261° with decomposition (its *ethyl ester* at 89°), is obtained from diphenyl-chloracetic ester by the action of silver (B. **22,** 1538). Its *nitrile*, melting at 215°, is formed by the interaction of the nitrile of diphenyl-acetic acid with sodium and iodine.

The dilactone of a **benzo-pinacone-o_2-dicarboxylic acid** $\overline{O.CO.C_6H_4C(C_6H_5).C(C_6H_5)C_6H_4CO}O$, melting at 265°, is formed on boiling o-benzoyl-benzoic acid with hydriodic acid and phosphorus (B. **29,** R. 498).

D. *ω, ω-Diphenyl-propane Group.*—**Dibenzyl-methane,** *α, γ-diphenyl-propane* $C_6H_5.CH_2.CH_2.CH_2.C_6H_5$, boiling at 290°–300°, results by the reducing action of hydriodic acid upon dibenzyl-ketone (see below).

α, γ-**Diphenyl-propylene** $C_6H_5CH_2.CH:CHC_6H_5$, b.p.$_{15}$ 179°, an oil with an odour of hyacinth, is formed from *α, γ*-diphenyl-propyl alcohol, b.p.$_{12}$ 193°, with anhydrous oxalic acid; also from *β*-bromo-dibenzyl-acetic acid by heating with dilute soda solution (B. **39,** 3046).

Tetraphenyl-allene $(C_6H_5)_2C:C:C(C_6H_5)_2$ (?), m.p. 164°, from the dry distillation of barium-diphenyl acetate (B. **39,** 1024).

Dibenzyl-ketone $C_6H_5.CH_2.CO.CH_2.C_6H_5$, melting at 40° and boiling at 330° (B. **24,** R. 946). This body is produced in the distillation of calcium-phenyl-acetate. *One* hydrogen atom of each of the two CH_2 groups can be replaced by alkyls. It condenses with oxalic ester and sodium ethylate to a *triketo*-R-*pentene* derivative, oxalyl-dibenzyl-ketone. With benzal-aniline it yields an addition product which takes various forms (C. 1899, II. 664). With PCl_5 it yields **1, 3-diphenyl-2-chloro-propylene** $C_6H_5CH_2.CCl:CHC_6H_5$, b.p.$_{12}$ 181°, and **di-iso-**

nitroso-dibenzyl-ketone $C_6H_5C(NOH).COC(NOH)C_6H_5$, with nitrous acid, m.p. 133° (B. **37**, 1134).

Sodium reduces dibenzyl-ketone to **dibenzyl-carbinol** $(C_6H_5.CH_2)_2CH.OH$, boiling at 327°. It combines to *dibenzyl-diphenol-methane* $(C_6H_5CH_2)_2C(C_6H_4OH)_2$ (B. **25**, 1271) with phenol.

Dibenzyl-phenyl-carbinol $(C_6H_5CH_2)_2C(OH)C_6H_5$, m.p. 87°, and **tribenzyl-carbinol** $(C_6H_5CH_2)_3C(OH)$, m.p. 115°, from benzoic acid ester and phenyl-acetic ester with two molecules $C_6H_5CH_2MgCl$ (B. **37**, 1456).

Benzyl-aceto-phenone $C_6H_5CH_2.CH_2.CO.C_6H_5$, m.p. 73°, is isomeric with dibenzyl-ketone. It is produced on reducing **benzylidene-aceto-phenone** $C_6H_5CH : CH.CO.C_6H_5$, m.p. 58°, b.p. 346°, with zinc dust and acetic acid. This latter compound is the condensation product of benzaldehyde and aceto-phenone. By means of sodium methylate it yields two stereo-isomeric oximes, m.p. 75° and 116°, the latter of which on Beckmann's transposition gives cinnamic anilide (A. **351**, 172). With HCl it unites to form **chloro-benzyl-aceto-phenone** $C_6H_5CHClCH_2COC_6H_5$; with bromine, a **dibromide** $C_6H_5CHBr.CHBr.COC_6H_5$, m.p. 157°, which, with alcoholic potash, yields monobromo-benzylidene aceto-phenone $C_6H_5.CBr : CHCOC_6H_5$, m.p. 44° (A. **308**, 219). The action of nitrous gases upon benzal-aceto-phenone gives various products, of which we may mention the sub-nitride $(C_{15}H_{12}O)N_2O_4$, which, on treatment with dilute soda, gives **benzal-nitro-aceto-phenone** $C_6H_5CH : C(NO_2)COC_6H_5$, m.p. 90°. The reduction of the latter with stannous chloride and HCl in methyl alcohol, produces **benzyl-iso-nitroso-aceto-phenone** $C_6H_5CH_2.C(NOH).COC_6H_5$, m.p. 126°, an oxime of the *diphenyl-diketo-propane* which is isomeric with dibenzoyl-methane (B. **36**, 3015; A. **340**, 63).

p_2-Dichloro-benzylidene-aceto-phenone, m.p. 157°, yields, with PCl_5 in benzene solution, a keto-chloride $ClC_6H_4CH : CH.CCl_2C_6H_4Cl$, m.p. 55°, in which one of the chlorine atoms occupies the middle position, is exceedingly mobile, and can easily be replaced by hydroxyl or methoxyl on treatment with moist silver oxide or methyl alcohol. The compounds dissolve in concentrated sulphuric acid with intense coloration (B. **42**, 1804) (cp. also dibenzylidene-acetone).

o-, m-, p-Oxy-benzylidene-aceto-phenone, from the corresponding oxy-benzaldehydes and aceto-phenone, melt at 154° with decomposition, at 160° and 183°.

The isomeric **benzylidene-o-, m-,** and **p-oxy-aceto-phenones,** m.p. 89°, 126°, and 173° respectively, are formed from benzaldehyde and the oxy-aceto-phenones. Coloration of the isomers, see B. **32**, 1921. Several poly-oxy-benzylidene-aceto-phenones are found in nature, usually in the form of glucosides.

Butein $(HO)_2[3, 4]C_6H_3CH : CH.COC_6H_3[2', 4'](OH)_2$, orange-yellow needles, m.p. 214°, as a glucoside in the flowers of *Butea frondosa*; this is split up on boiling with potash into proto-catechuic acid and resaceto-phenone (C. 1904, II. 451). **Naringenin** $HO[4]C_6H_4CH : CH.COC_6H_2[2', 4', 6'](OH)_3$, m.p. 248°, and **hesperitin** $(HO)[3](CH_3O)[4]C_6H_3CH : CH.COC_6H_2[2', 4', 6'](OH)_3$, m.p. 224°, are formed by breaking up the glucosides naringin and hesperidin (*q.v.*) with dilute acids, On boiling with potash they yield phloro-glucin and p-cumaric acid and iso-ferulic acid respectively. Isomers of hesperitin are **homo-eriodictyol** $HO[4](CH_3O)[3]C_6H_3CH : CH.COC_6H_2[2', 4', 6'](OH_3)$, b.p.

223°, and **eriodictyol** $(HO)_2[3,4]C_6H_3CH : CH.COC_6H_2[2',4',6'](OH)_3$, m.p. 267°, from the leaves of *Eriodictyon californicum* (C. 1911, I. 150). On boiling with mineral acids the benzylidene-o-oxy-aceto-phenones are transformed into the isomeric flavanones $C_6H_4\begin{cases}O—CH.C_6H_5\\CO.CH_2\end{cases}$, a reaction which has been used for the synthesis of numerous vegetable dyes belonging to this group; cp. quercetrin, fisetin, luteolin, etc.

Alcoholic potash converts acety-o-oxy-benzylidene-aceto-phenone into *benzoyl-cumarone* (*q.v.*) $C_6H_4\begin{cases}O\\CH\end{cases}C.CO.C_6H_5$. Reduction changes o-oxy-benzylidene-aceto-phenone into **α-phenyl-γ-(o-oxy-phenyl)-propyl alcohol** $HO.C_6H_4.CH_2.CH_2.CH(OH)—C_6H_5$, m.p. 97°, which is condensed by HCl in methyl alcohol to **α-phenyl-cumaran** $C_6H_4\begin{cases}CH_2.CH_2\\O—CH.C_6H_5\end{cases}$ (B. **29**, 244, 375).

o-Oxy-styryl-diphenyl-carbinol $HO[2]C_6H_4CH : CHC(OH)(C_6H_5)_2$, m.p. 164°–166°, from cumarin with two molecules C_6H_5MgBr (C. 1903, I. 1179; B. **37**, 496).

The condensation of two molecules of aceto-phenone by heat alone, or by zinc ethide or zinc chloride, yields a homologue of benzal-aceto-phenone called **dypnone** $C_6H_5.C(CH_3) : CH.COC_6H_5$, m.p. 225° (22 mm.), which sustains the same relation to aceto-phenone as mesityl oxide bears to acetone (B. **27**, R. 339); heating splits up dypnone with formation of unsaturated hydrocarbons, diphenyl-furfurane, and triphenyl-benzol (C. 1899, II. 96). On standing in alcoholic solution, dypnone combines with hydroxylamine to form **dypnone-hydroxylamine** $C_6H_5C(CH_3)(NHOH).CH_2COC_6H_5$, m.p. 110°; under other conditions two dypnone oximes are formed, $C_6H_5C(CH_3) : CHC(NOH)C_6H_5$, m.p. 78° and 134°, the latter of which yields by Beckmann's transposition the anilide of β-methyl-cinnamic acid (B. **37**, 730).

Benzaldehyde condenses as readily as aceto-phenone with desoxy-benzoïn under the influence of alkalies, forming **benzylidene-desoxy-benzoïn** $C_6H_5CH : C(C_6H_5)CO.C_6H_5$, m.p. 101°; this is also formed from benzamarone by distillation, besides iso-benzylidene-desoxy-benzoïn, m.p. 89°. The latter is easily converted into the isomeride of higher melting-point. It is also formed by condensation of benzaldehyde and desoxy-benzoïn by means of HCl and chloro-benzyl-desoxy-benzoïn, m.p. 172°, which is easily converted by alkalies into benzal-desoxy-benzoïn, m.p. 101°; but it is split up by distillation into stilbene and benzoyl chloride (B. **26**, 447, 818; **34**, 3897; **35**, 3865):

$$\begin{matrix}C_6H_5CH\\C_6H_5\dot{C}COC_6H_5\end{matrix} \longleftarrow \begin{matrix}C_6H_5CHCl\\C_6H_5\dot{C}HCOC_6H_5\end{matrix} \longrightarrow \begin{matrix}C_6H_5\dot{C}H\\C_6H_5\dot{C}H\end{matrix} + \begin{matrix}Cl\\\dot{C}OC_6H_5\end{matrix}$$

By reduction, benzal-desoxy-benzoïn yields **benzyl-desoxy-benzoïn** $C_6H_5.CH_2.CH(C_6H_5)COC_6H_5$, m.p. 120°, which can also be obtained direct by benzylating desoxy-benzoïn.

ββ-Diphenyl-propio-phenone $C_6H_5COCH_2.CH(C_6H_5)_2$, m.p. 96°, by attachment of one molecule phenyl-magnesium bromide to benzal-aceto-phenone (C. 1904, II. 445). Correspondingly, we obtain from phenyl-magnesium bromide and benzylidene-desoxy-benzoïn in ether solution:

α, β, β - Triphenyl- propio - phenone $C_6H_5COCH(C_6H_5)CH(C_6H_5)_2$,

m.p. 182°, which is also formed from α-phenyl-cinnamic ester with gases of phenyl-magnesium bromide. In ligroïn solution it is found possible to isolate, as the first addition product, the **tetraphenyl-propinol** $C_6H_5C(OH):C(C_6H_5)CH(C_6H_5)_2$, which, at 95°–100°, melts with transformation into triphenyl-propio-phenone. It greedily absorbs oxygen, with formation of a peroxide, m.p. 127°, which, on heating, decomposes into diphenyl-aceto-phenone and benzoic acid (C. 1906, II. 1059).

Benzoyl-dibenzyl-methane, *dibenzyl-aceto-phenone* $C_6H_5COCH(CH_2C_6H_5)_2$, m.p. 78°, is formed by heating aceto-phenone with benzyl chloride and caustic potash to 160°–170° (A. **310,** 322).

By condensation of o-phthal-aldehydic acid with aceto-phenone we obtain **phenacyl-phthalide** $C_6H_4\begin{cases}CHCH_2COC_6H_5\\ \diagdown\!\!\diagup\\ COO\end{cases}$, m.p. 182° (C. 1898, II. 980).

Benzoyl-phenyl-acetylene $C_6H_5COC:CC_6H_5$, m.p. 50°, from sodium-phenyl-acetylene and benzoyl chloride in ether. This is split up by alkalies into aceto-phenone and benzoic acid, and by concentrated sulphuric acid into dibenzoyl-methane (A. **308,** 276; C. 1900, I. 1290). **Phenyl-acetylene-phenyl-carbinol** $C_6H_5C:C.CH(OH)C_6H_5$, b.p. 221°, from sodium-phenyl-acetylene and benzaldehyde (C. 1902, I. 629).

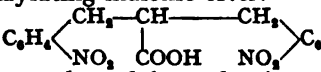
Dibenzoyl-methane $C_6H_5CO.CH_2.COC_6H_5$ or $C_6H_5C(OH):CHCOC_6H_5$ (cp. *Proc. Chem. Soc.*, **20,** 48), m.p. 81°, is formed by boiling dibenzoyl-acetic ester with water, by condensation of benzoic acid ester and aceto-phenone, or by transposition of the aceto-phenone-O-benzoate $C_6H_5C(OCOC_6H_5):CH_2$ obtained from aceto-phenone by heating with benzoyl chloride, the transposition being effected by boiling with sodium in benzene solution (B. **36,** 3674). It is soluble in alkali, forms a sparsely soluble copper salt and a red iron salt, and is easily attacked by potassium permanganate. On treatment with benzoyl chloride and pyridin it yields an *O-benzoate* $C_6H_5C(OCOC_6H_5):CHCOC_6H_5$, m.p. 109° (B. **36,** 3679). Nitrous acid converts it into an *iso-nitroso-derivative* $(C_6H_5.CO)_2C:N.OH$, which may be converted into the corresponding **diphenyl-triketone** $C_6H_5.CO.CO.CO.C_6H_5$, b.p. 289°, (175 mm. pressure). It solidifies to a golden-yellow mass, melting at 70°. It combines with water to a colourless hydrate (B. **23,** 3378).

Dibenzoyl-acetyl-methane, *dibenzoyl-acetone*, occurs in two forms, one of which probably represents the *diketo-hydroxyl* form $(C_6H_5.CO)_2C:C(OH)CH_3$ (α-, m.p. 80°), the other the *triketo* form $(C_6H_5CO)_2.CH.COCH_3$ (β-, m.p. 107°–110°). It results from benzoyl-acetone and benzoyl chloride with soda. Similarly, dibenzoyl-methane yields (β)-**tribenzoyl-methane** $(C_6H_5CO)_3CH$, m.p. 225°. By boiling with potash and acetic ester this β-modification is changed to the α-form $(C_6H_5CO)_2C:C(OH)C_6H_5$, soluble in alkalies (A. **291,** 25). The latter combines with one molecule diazo-benzol chloride to form a yellow diazo-oxy-compound (1), m.p. 125°, which is easily split up by mineral acids. On heating, it first turns into the red *C-azo-compound* (2), m.p. 164°, stable in the presence of acids, and further, by migration of a benzoyl group, into the colourless benzoyl-phenyl-hydrazone of diphenyl-triketone (3), m.p. 203° (B. **41,** 4012):

$$(C_6H_5CO)_2:C \qquad \longrightarrow \qquad (C_6H_5CO)_2:C.N:NC_6H_5 \qquad \longrightarrow \qquad (C_6H_5CO)_2:C:N.NC_6H_5$$
$$(1)\quad C_6H_5C.O.N:NC_6H_5 \qquad (2)\quad C_6H_5\,CO \qquad (3)\quad C_6H_5\,CO$$

This process corresponds to the transposition of fatty aromatic azo-compounds into aryl-hydrazones, and to a reversal of the conversion of the quinone-acyl-phenyl-hydrazones into O-acylated oxy-azo-compounds.

Carboxylic Acids.—**Dibenzyl-acetic acid** $(C_6H_5.CH_2)_2CH.COOH$, m.p. 87°, is formed from **α-benzyl-cinnamic acid** $C_6H_5CH : C(CH_2C_6H_5)COOH$, m.p. 159°, the condensation product of benzaldehyde with hydrocinnamic acid by reduction with Na amalgam (*J. pr. Ch.* 2, **62**, 545). It is also derived from **dibenzyl-malonic acid** $(C_6H_5CH_2)_2C(COOH)_2$, the *ester* of which is produced by benzylating malonic ester.

o, o-Dinitro-benzyl-acetic acid  made in an analogous manner, may be condensed by reduction with zinc dust to *tetrahydro-naphthinolin* (*q.v.*) (B. **27**, 2248; **29**, 636).

Dibenzoyl-malo-nitrile $(C_6H_5CH_2)C(CN)_2$, m.p. 130° and b.p. 360°, is obtained from the corresponding nitrilo-acid amide, which is prepared from cyanacetamide. Sodium and alcohol reduce the nitrile with elimination of a cyanogen group to **dibenzyl-ethylamine** $(C_6H_5CH_2)_2CH.CH_2.NH_2$, whose *hydrochloride* melts at 190° (B. **29**, R. 1111).

Dibenzyl-glycolic acid $(C_6H_5.CH_2)_2C(OH).CO_2H$, **oxatolylic acid,** is produced by saponification of its nitrile, the HCN addition product of dibenzyl-ketone, and when vulpic and pulvic acids are boiled with dilute alkalies. It melts at 156°. When boiled with concentrated potassium hydroxide it decomposes into oxalic acid and two molecules of toluol (A. **219**, 41).

α-Phenyl-β-benzoyl-propionic acid, *phenyl-phenacyl-acetic acid,* $C_6H_5CO.CH_2.CH(C_6H_5)COOH$, melts at 153°. Its *nitrile* melts at 127°. Its ester is formed from phenyl-succinic-α-methyl ester acid chloride with benzene and $AlCl_3$. The acid is produced when CNK acts upon chloro-benzyl-aceto-phenone. If heated with acetic anhydride it yields the *lactone* of isomeric **α, γ-diphenyl-γ-oxy-crotonic acid** $C_6H_5C(O) : CH.CH(C_6H_5)CO$, melting at 110°, while upon reduction with sodium amalgam, **α, γ-diphenyl-butyro-lactone** $C_6H_5.CH(O).CH_2.CH(C_6H_5)CO$ (A. **284**, 1).

α, γ-Diphenyl-aceto-acetic acid is isomeric with phenyl-phenacyl-acetic acid. Its *ester*, $C_6H_5.CH_2.CO.CH(C_6H_5)CO_2C_2H_5$, melting at 79°, is formed when two molecules of phenyl-acetic ester are condensed with sodium ethylate. Concentrated sulphuric acid condenses the ester to a naphthalene derivative—phenyl-naphtho-resorcinol (A. **296**, 1.)

β-Phenyl-γ-benzoyl-butyric acid $C_6H_5CO.CH_2.CH(C_6H_5).CH_2.COOH$, m.p. 153°, is formed by attachment of aceto-phenone to cinnamic ester, by means of sodium ethylate, and by transformation of the addition product of malonic ester and benzylidene-aceto-phenone (B. **34**, 653).

Benzylidene-benzoyl-acetic ester, m.p. 98°, from benzaldehyde, benzoyl-acetic ester, and piperidin (C. 1903, I. 1420; II. 1270).

Dibenzoyl-acetic acid $(C_6H_5.CO)_2CH.COOH$ melts at 109°. Its *ester*, from benzoyl-acetic ester and benzoyl chloride, yields CO_2 and dibenzyl-methane by dry distillation, and aceto-phenone, carbon dioxide, and benzoic acid when digested with sulphuric acid. Its *nitrile*, obtained from cyan-aceto-phenone with benzoyl chloride, shows

very acid properties. The silver salt gives, with methyl iodide and methyl ether, $C_6H_5COC(CN) : C(OCH_3)C_6H_5$, m.p. 118°; with benzoyl-chloride, tribenzoyl-aceto-nitrile $(C_6H_5CO)_3C.CN$ or $C_6H_5COC(CN) : C(OCOC_6H_5)C_6H_5$, m.p. 138° (*J. pr. Ch.* 2, **58**, 151).

γ-Phenyl-β-benzylidene-α-keto-butyro-lactone $\begin{matrix} C_6H_5CH—O \\ C_6H_5CH : C—CO \end{matrix}\!\!>\!\!CO$, m.p. 167°; this keto-lactone, in the form of yellow crystals, is obtained by condensation of two molecules benzaldehyde with pyro-racemic acid by means of gaseous HCl (B. **32**, 1450; **34**, 817); on reduction with sodium amalgam it gives **γ-phenyl-β-benzyl-keto-butyro-lactone,** in two modifications, m.p. 134° and 137° (also from benzyl-pyro-racemic acid with benzaldehyde). The isomeric **β-phenyl-γ-benzyl-α-keto-butyro-lactone,** m.p. 171°, is formed from two molecules phenyl-pyro-racemic acid with rejection of CO_2 (B. **35**, 1942).

γ-Benzyl-γ-benzylidene-pyro-racemic acid $\begin{matrix} C_6H_5CH_2 \\ C_6H_5CH \end{matrix}\!\!>\!\!C.CH\!<\!\!\begin{matrix} COOH \\ CH_2COOH \end{matrix}$, m.p. 147°; its ester is formed by condensation of dibenzyl-ketone and succinic ester by sodium alcoholate (A. **308**, 175).

γ-Phenyl-γ-phenacyl-pyro-racemic acid $\begin{matrix} C_6H_5COCH_2 \\ C_6H_5 \end{matrix}\!\!>\!\!CH.CH\!<\!\!\begin{matrix} CH_2COOH \\ COOH \end{matrix}$ from succinic acid ester and benzal aceto-phenone by means of $NaOC_2H_5$; its dimethyl ester is easily further condensed to pentacyclic diketone-carboxylic ester $\begin{matrix} C_6H_5CO.CH.CO.CH_2 \\ C_6H_5CH——CHCO_2CH_3 \end{matrix}$, which is in turn easily split up by sodium methylate to an acyclic dimethyl ester (A. **326**, 347).

α, β, γ-**Triphenyl-glutaric acid** $C_6H_5CH[CH(C_6C_5)COOH]_2$, m.p. 237°; the *nitrile*, m.p. 138°, of this acid is formed by the combination of benzal-benzyl cyanide with the second molecule of benzyl cyanide (B. **31**, 3059).

E. *ω, ω-Diphenyl-butane Group.*—**Dibenzyl-ethane,** α, δ-**diphenyl-butane** $C_6H_5.CH_2.CH_2.CH_2.CH_2.C_6H_5$, melting at 52°, is formed by the reduction of Δ^2-**diphenyl-butylene** $C_6H_5.CH : CH.CH_2.CH_2.C_6H_5$, which is produced from diphenyl-butadiene and diphenyl-butenin with Na amalgam (A. **342**, 253), or from α-phenyl-cinnamenyl-acrylic acid nitrile with Na and alcohol (B. **23**, 2857).

α, δ-**Diphenyl-butadiene,** *diphenyl-diethylene* $C_6H_5CH : CH.CH : CHC_6H_5$, is known in its three theoretically possible stereo-isomeric forms: α-form (trans-trans), m.p. 151°; β-form (cis-cis), m.p. 70·5°; γ-form (cis-trans), oily. Of these the α-form is most stable, and the other forms pass into it on standing, and do so rapidly in sunlight. The α-form is obtained (1) by heating α-phenyl-cinnamenyl-acrylic acid or dibenzal-propionic acid; (2) from the dibromide of Δ^2-diphenyl-butylene by means of quinolin; (3) in small quantity on reduction of phenyl-acetylene with zinc dust and alcohol; (4) by the action of magnesium upon ω-bromo-styrol (B. **43**, 1232). The β-form is obtained from diphenyl-diacetylene, the γ-form from diphenyl-butenin (m.p. 97°) by reduction with zinc dust and alcohol (A. **342**, 238). With bromine in chloroform the diphenyl-butadiene gives dibromide, m.p. 141°, which is also obtained by attachment of two molecules HBr of diphenyl-butenin, and probably contains the bromine atoms in the 1, 4-position (A. **342**, 244). With two molecules NO_2 it also combines with 1, 4-addition to **diphenyl-dinitro-butylene** $C_6H_5CH(NO_2).CH : CH.CH(NO_2)C_6H_5$, m.p. 158°, colourless needles from which, by action of alkalies,

nitrous acid is split off to form **diphenyl-α-nitro-butadiene** $C_6H_5C(NO_2)$: CH.CH : CHC_6H_5, m.p. 112°, in golden-yellow columns (A. **360**, 299).

Diphenyl-butenin C_6H_5CH : CH.C : CC_6H_5 also occurs in two stereo-isomeric forms, of which the stable trans-form, m.p. 97°, is formed by solution of phenyl-acetylene-copper in glacial acetic acid, and the unstable liquid cis-form, b.p.$_{12}$ 188°, by partial reduction of diphenyl-diacetylene with zinc dust and alcohol. Illumination or traces of iodine convert the unstable form into the stable form (A. **342**, 225).

Diphenyl-diacetylene $C_6H_5C : C.C : C.C_6H_5$, melting at 88°. This is made by shaking copper phenyl-acetylide $C_6H_5C : C.Cu$ in ammoniacal solution with air, or by the action of potassium ferricyanide. *It is the parent hydrocarbon of indigo-blue.* Its *o, o-dinitro-derivative* $C_6H_4\langle^{C:C.C:C}_{NO_2\ O_2N}\rangle C_6H_4$ (from o-nitro-phenyl-acetylene) is rearranged by concentrated sulphuric acid into the isomeric di-isatogen (*q.v.*), which becomes indigo-blue : $C_6H_4\langle^{CO}_{NH}\rangle C : C\langle^{CO}_{NH}\rangle C_6H_4$, by reduction with ammonium sulphide (B. **15**, 53).

The action of Br in CS_2 solution produces a dibromide, m.p. 42°, and a tetrabromide, m.p. 173°; but bromination in ether or acetic acid solution produces ring-closure and tribromo-phenyl-naphthalin (A. **342**, 229).

α, α, δ-**Triphenyl-butadiene** $(C_6H_5)_2C$: CH.CH : CHC_6H_5, m.p. 102°, and α, α, β, δ-**tetraphenyl-butadiene** $(C_6H_5)_2C$: $C(C_6H_5)$.CH : CHC_6H_5, m.p. 147°, are formed by attaching diphenyl-ketone to cinnamic aldehyde and benzal-aceto-phenone respectively, with rejection of CO_2 (B. **42**, 4249).

α, α, δ, δ-**Tetraphenyl-butadiene** $(C_6H_5)_2C$: CH.CH.C : $C(C_6H_5)_2$, m.p. 202°, from **tetraphenyl-tetramethylene-glycol** $(C_6H_5)_2C(OH).CH_2.CH_2.C(OH)(C_6H_5)_2$, m.p. 208°, the condensation product of succinic ester with phenyl-magnesium bromide (C. 1903, I. 967).

Ketones.—**Phenethyl-benzyl-ketone,** 1, 4-*diphenyl-butanone* $C_6H_5.CH_2.CH_2.CO.CH_2.C_6H_5$, boiling at 234°–238°, is produced when hydrocornicularic acid is distilled with lime; also by distillation of calcium-phenyl acetate and hydro-cinnamate. It is obtained pure by the reduction of **1, 4-diphenyl-butenone,** *styryl-benzyl-ketone* $C_6H_5CH : CHCOCH_2C_6H_5$, m.p. 71°, formed from benzaldehyde and phenyl-acetone by alkaline condensation (M. **22**, 659, 749).

Phenyl-iso-crotone-phenone $C_6H_5CO.CH_2.CH : CHC_6H_5$, m.p. 93°, is obtained by the reduction of diphenyl-α-nitro-butadiene with $SnCl_2$ and HCl; it dissolves in alkalies with formation of salts of diphenyl-oxy-butadiene $C_6H_5C(OH)$: CH.CH : CHC_6H_5; with benzaldehyde, it condenses and forms **dibenzal-propio-phenone** $C_6H_5COC(:CHC_6H_5).CH : CHC_6H_5$, m.p. 117° (B. **40**, 4825). **o-Oxy-styryl-benzyl-ketone** HO[1] C_6H_4CH : $CHCOCH_2C_6H_5$, b.p.$_{12}$ 217°–219°, from cumarin with benzyl-magnesium chloride (B. **37**, 498).

Diphenacyl, *dibenzoyl-ethane* $C_6H_5CO.CH_2.CH_2.COC_6H_5$, m.p. 145°, from phenacyl-benzoyl-acetic ester by ketone-splitting, and by reduction of dibenzoyl-ethylene and various halogen diphenacyls; as a γ-diketone it easily forms *diphenyl-furfurane, thiophene,* and *pyrrol.*

γ-**Chloro-** and γ-**bromo-diphenacyl** $C_6H_5COCHCl.CH_2COC_6H_5$ and $C_6H_5COCHBr.CH_2COC_6H_5$, m.p. 141° and 139°, are formed from dibenzoyl-ethylene with halogen hydrides, which are easily split off; with

potassium iodide they are easily transposed to **γ-iodo-diphenacyl** $C_6H_5COCHI.CH_2COC_6H_5$, m.p. 121°. Isomeric halogen diphenacyls are formed by the action of alcoholic potash upon phenacyl haloids, $C_6H_5COCH_2X$; in contrast with the above compounds they show no ketone or diketone reactions and are marked by the ease of addition of carboxylic acid haloids and halogen hydrides. They are regarded as the various stereo-isomeric forms of the corresponding di-enol forms of the halogen diphenacyls $C_6HC(OH) : CX.CH : C(OH)C_6H_5$. On reduction they yield diphenacyl. **α- and β-Chloro-diphenacyl**, m.p. 117° and 155°, **α- and β-bromo-diphenacyl**, m.p. 129° and 161°, **α-, β-, and δ-iodo-diphenacyl**, m.p. 82°–83° with decomposition, m.p. 113° with decomposition, and m.p. 150°–153° with decomposition. If metallic sodium is made to act upon the ether solution of phenacyl iodide, we obtain **tribenzoyl-trimethylene** $C_6H_5COCH\langle^{CHCOC_6H_5}_{CHCOC_6H_5}$ (B. **36**, 2386, 2425).

Dibenzoyl-ethylene $C_6H_5COCH : CHCOC_6H_5$, cis-form, m.p. 134°, trans-form, m.p. 111°, is produced by heating dibenzoyl-malic acid, which splits off $2CO_2$ and H_2O. The cis-form is converted by HCl into the trans-form, and the latter, by illumination, back into the cis-form. The cis-form reacts more easily than the trans-form with hydrazin, forming *diphenyl-pyridazin*, and it also forms addition products more readily (B. **35**, 168).

Phenacyl-benzyl-ketone $C_6H_5COCH_2COCH_2C_6H_5$, m.p. 54°–56°, from phenyl-acetic ester and aceto-phenone with sodium in ether. It is isomeric with diphenacyl (B. **34**, 1479).

Desyl-aceto-phenone, *α, β-dibenzoyl-phenyl-ethane* $C_6H_5CO.CH(C_6H_5).CH_2.COC_6H_5$, melting at 126°, is produced in the condensation of benzoïn and aceto-phenone with potassium cyanide (B. **23**, R. 636; **26**, 60). See B. **29**, R. 171, for the action of hydrazin.

Bidesyl $\begin{matrix}C_6H_5.COCH.C_6H_5\\ |\\ C_6H_5.CO.CH.C_6H_5\end{matrix}$, *dibenzoyl-dibenzyl*, results when desyl-bromide or iodine acts upon sodium desoxy-benzoïn (B. **21**, 1355; **25**, 285). It melts at 255°. **Iso-bidesyl**, formed simultaneously, melts at 161°. Bidesyl yields tetraphenyl-pyrrol and tetraphenyl-furfurane, the so-called *lepidene*.

α,β-Dibenzoyl-styrol, *anhydro-aceto-phenone-benzile* $C_6H_5CO.CH : C(C_6H_5)COC_6H_5$, m.p. 129°, is obtained from benzile and aceto-phenone by the action of caustic potash. When heated it rearranges itself by the migration of a phenyl group into the isomeric **triphenyl-croto-lactone**, m.p. 118°:

$$\underset{\text{Dibenzoyl-styrol}}{C_6H_5CO.C(C_6H_5) : CHCOC_6H_5} \longrightarrow \underset{\alpha,\alpha,\gamma\text{-Triphenyl-croto-lactone.}}{\overline{CO.C(C_6H_5)_2.CH : C(O)}C_6H_5}$$

Dibenzoyl-stilbene, *acicular oxy-lepidene* $C_6H_5CO.C(C_6H_5) : C(C_6H_5)COC_6H_5$, m.p. 220°, resulting from the oxidation of lepidene (see above) with nitric acid, or of thio-nessal with potassium chlorate and hydrochloric acid, also yields, on heating, **tetraphenyl-croto-lactone**, *tabular oxy-lepidene*, m.p. 136°:

$$\underset{\text{Dibenzoyl-stilbene}}{C_6H_5COC(C_6H_5) : C(C_6H_5)COC_6H_5} \longrightarrow \underset{\alpha,\alpha,\beta,\gamma\text{-Tetraphenyl-croto-lactone}}{\overline{COC(C_6H_5)_2.C(C_6H_5 :)C(O)}C_6H_5}.$$

Bidesyl results from the reduction of dibenzoyl-stilbene.

Diphenyl-tetraketone $C_6H_5.CO.CO.CO.CO.C_6H_5(+H_2O)$, m.p. 87°, is red in colour when hydrous and yellow when anhydrous. It is formed in the oxidation of **benzoyl-formoin** $C_6H_5.CO.CO.CH(OH)COC_6H_5$, m.p. 170°, which is produced, like benzoin, from benzaldehyde by condensing two molecules of phenyl-glyoxal with potassium cyanide. Benzoyl-formoin also results readily from the action of soda upon iso-nitroso-aceto-phenone acetate $C_6H_5.CO.CH : NO.COCH_3$. Substituted diphenyl-tetraketones have been similarly prepared (B. **25,** 3468).

Diphenyl-tetraketone is a member of the following CO homologous series :

Diphenyl-ketone, benzo-phenone	$C_6H_5COC_6H_5$
Diphenyl-diketone, benzile	$C_6H_5COCOC_6H_5$
Diphenyl-triketone	$C_6H_5COCOCOC_6H_5$
Diphenyl-tetraketone	$C_6H_5COCOCOCOC_6H_5$.

Hydroxylamine forms but one 1, 4-*dioxime* $[C_6H_5C(NOH)CO]_2$, m.p. 176° with decomposition ; the 2, 3-*dioxime* or *dibenzoyl-glyoxime* $C_6H_5.COC(NOH)C(NOH)CO.C_6H_5$, m.p. 108° with decomposition, results from the reduction of its peroxide, which is formed in the interaction of nitric acid and aceto-phenone. Hydroxylamine converts the 2, 3-dioxime into **diphenyl-tetraketoxime** $C_6H_5[C(NOH)]_4C_6H_5$, m.p. 225° (B. **26,** 528).

Carboxylic Acids.—From diphenyl-butadiene the following two acids are derived :

α-Phenyl-cinnamenyl-acrylic acid, *cinnamylidene-phenyl-acetic acid* $C_6H_5C(CO_2H) : CH.CH : CHC_6H_5$, m.p. 188°, from cinnamic aldehyde and phenyl-acetic acid, and **dibenzal-propionic acid** $C_6H_5CH : C(COOH).CH : CHC_6H_5$, obtained from benzaldehyde and γ-phenyl-iso-crotonic acid by Perkin's synthesis. These two diolefin-carboxylic acids have been closely examined by Thiele, as they furnished material for his theory of conjugate double bindings (A. **306,** 87–246 ; but see B. **37,** 1121).

The α-phenyl-cinnamenyl-acrylic acid gives with bromine a dibromide, m.p. 175° with decomposition, containing the Br atoms in the 1, 4-position, since with alkali it yields α, α-diphenyl-dihydro-furfurane and a brominated acid. On the other hand, the dibromide heated with diethyl-aniline is transposed into the lactone of **cornicularic acid** $C_6H_5C(COOH) : CH.COCH_2C_6H_5$, m.p. 123°, which is also produced by the reduction of vulpic acid. The reduction of phenyl-cinnamenyl-acrylic acid produces first **2, 5-diphenyl-pentenic-acid** $C_6H_5CH(COOH)CH : CHCH_2C_6H_5$, m.p. 101°, which with alkali is isomerised to the α, β-unsaturated acid, and with glacial acetic sulphuric acid to the lactone of **tetrahydro-cornicularic acid** $C_6H_5CH(COOH)CH_2.CH(OH)CH_2C_6H_5$. Bromine converts the 2, 5-diphenyl-pentenic acid into **1, 3-phenyl-benzyl-Δ¹-croto-lactone** $C_6H_5C : CH.CH.CH_2C_6H_5$ (CO—O), which with alkali yields hydro-cornicularic acid (A. **319,** 211).

Dibenzal-propionic acid also yields a 1, 5-dibromide, which is easily converted into bromo-lactone and a diolefin-lactone : **benzal-phenyl-croto-lactone** $C_6H_5CH : C.CH : CC_6H_5$ (CO—O), m.p. 150°. **α-Phenacyl-cinnamic acid** $C_6H_5CH : C(COOH)CH_2COC_6H_5$, m.p. 171°, is produced from the

former by alkali. Reduction of the bromo-lactone and diolefin-lactone gives an unstable lactone (1), m.p. 101°, and a stable lactone (2), m.p. 67°, both of which yield with alkali **α-phenacyl-hydro-cinnamic acid** (3) :

(1) $C_6H_5CH_2.\dot{C}H.CH:\dot{C}C_6H_5$ — CO——O ⟶ (3) $C_6H_5CH_2\dot{C}HCH_2COC_6H_5$ ⟵ (2) $C_6H_5CH_2\dot{C}:CH.\dot{C}HC_6H_5$ — CO——O

Reduction of diphenyl-propionic acid gives **α-benzyl-phenyl-iso-crotonic acid** $C_6H_5.CH_2CH(COOH)CH:CHC_6H_5$, m.p. 124°, distinguished by the ease with which it produces naphthalin derivatives. With bromine it splits off HBr and produces *phenyl-bromo-tetrahydro-naphthoic acid.*

From the nitrile of cinnamenyl-phenyl-acrylic acid is derived **p_2-diamido-diphenyl-cyano-butadiene** $NH_2[4]C_6H_4CH:CH.CH:C(CN)C_6H_4[4]NH_2$, m.p. 196°, which, like benzidin and p_2-diamido-stilbene, is a generator of substantive cotton dyes (B. **34,** 3109).

Diphenyl-butadiene-acetic acid $C_6H_5CH:CH.CH:C(C_6H_5)CH_2COOH$, m.p. 190°, from cinnamic aldehyde and phenyl-succinic acid, on boiling with acetic anhydride, yields *diphenyl-phenol* (B. **36,** 1407).

The ester of **benzoyl-phenacyl-acetic acid, α, β-dibenzoyl-propionic acid** $C_6H_5.CO.CH_2.CH(CO.C_6H_5)COOR$, is obtained from benzoyl-acetic ester with phenacyl bromide. In the ketone decomposition it yields diphenacyl ; and by the acid decomposition, benzoyl-propionic acid and benzoic acid. **Iso-oxalyl-dibenzyl-ketone,** melting at 240°–242°, may be referred to benzoyl-oxalyl-phenyl-acetic acid $C_6H_5.CH_2.CO.CO.CH(C_6H_5).COOH$, isomeric with dibenzoyl-propionic acid. It is formed on heating oxalyl-dibenzyl-ketone beyond its melting-point (A. **284,** 293) :

$$C_6H_5C:C(OH).CO.CH.C_6H_5 \longrightarrow C_6H_5C:C(OH).C:CH.C_6H_5$$
$$\quad\quad\quad

dicarboxylic ester. The esters of the acid appear in three forms, of which the unstable variety, soluble in alkalies, is probably the enol-form $C_6H_5C(OH):C(COOH):C(COOH):C(OH)C_6H_5$, while the other two represent the syn- and anti-modifications of the keto-form (B. **29**, R. 962).

Dibenzoyl-maleic acid ester $\begin{matrix}C_6H_5COCCO_2C_2H_5\\C_6H_5COCCO_2C_2H_5\end{matrix}$, m.p. 75°, from disodium-dibenzoyl-succinic acid ester with iodine, is transposed by heat into **dibenzoyl-fumaric acid** $\begin{matrix}C_6H_5COCCO_2C_6H_5\\CO_2C_2H_5CCOC_6H_5\end{matrix}$, m.p. 88°. The maleinoid ester condenses more easily than the fumaroid with hydrazin to form diphenyl-pyridazin-carboxylic ester (*q.v.*). The potassium salts produced by the acidulation of the esters give, on acidulation, a hydrate of dibenzoyl-ethylene-dicarboxylic acid, the so-called **dibenzoyl-malic acid** $\begin{matrix}C_6H_5COC(OH)CO_2H\\C_6H_5COCHCO_2H\end{matrix}$ (?), which on heating loses water and $2CO_2$, and passes into dibenzoyl-ethylene (B. **33**, 3784).

Diphenyl-oxalyl-diacetic acid, *diphenyl-ketipic acid* $COOH.CH(C_6H_5)CO.CO.CH(C_6H_5)COOH$ is isomeric with dibenzoyl-succinic acid. Its *dinitrile*, melting at 270° with decomposition, is produced by the condensation of oxalic ester with two molecules of benzyl cyanide. When saponified with hydrochloric or sulphuric acid it yields not the free acid, but passes at once into its anhydride, a *monolactone*, **pulvic acid** $\overline{OOC.CH(C_6H_5)CO.C}:C(C_6H_5)COOH$, melting at 214°, and a *dilactone* $\overline{OOC.C(C_6H_5)}:\overline{C.C}:C(C_6H_5)COO$. Pulvic acid may also be prepared from **vulpic acid,** $C_{19}H_{14}O_5$, consisting of yellow prisms, melting at 110°, and found in a certain moss and in the lichen *Cetraria vulpina*, by boiling it with lime-water. Sodium ethylate converts pulvic acid back into salts of vulpic acid. The latter is therefore very probably to be regarded as a methyl ether of pulvic acid (B. **27**, R. 869; A. **288**, 14). Zinc dust and ammonia reduce pulvic acid to **hydro-cornicularic acid,** *α, δ-diphenyl-lævulinic acid* $C_6H_5.CH_2.CO.CH_2.CH(C_6H_5)COOH$, melting at 134°. Distilled with lime, it yields phenyl-ethyl-benzyl-ketone, and when heated with caustic potash the products are toluene and phenyl-succinic acid. Boiling alkalies decompose pulvic and vulpic acids into $2CO_2$ and dibenzyl-glycollic acid. If it be assumed that diphenyl-ketipic acid is formed at first, then this reaction, discarding the evolution of CO_2, is an analogue of the benzilic acid transposition :

$$\begin{matrix}C_6H_5.CH(COOH).CO\\C_6H_5.CH(COOH).CO\end{matrix}\xrightarrow[-2CO_2]{+H_2O}\begin{matrix}C_6H_5.CH_2\\C_6H_5.CH_2\end{matrix}\!\!>\!C(OH)COOH.$$

Ethane-dibenzoyl-o_2-dicarboxylic acid $COOH.C_6H_4CO.CH_2.CH_2CO.C_6H_4.COOH$, is another isomeride of dibenzoyl-succinic acid. It melts at 166°. It is made by boiling **ethine-diphthalyl** $\overline{O.OC.C_6H_4.C}:CH.CH:\overline{C.C_6H_4.COO}$, melting above 350°, the *dilactone* corresponding to it, with alkalies. Ethine-diphthalyl results from the condensation of two molecules of phthalic anhydride with succinic acid when two molecules of carbon dioxide are split off (B. **17**, 2770). Sodium alcoholate rearranges it into bis-diketo-hydrindene.

F. *ω,ω-Diphenyl-pentane Group.* — **γ-Diphenyl-methylene-α,**

ϵ-diphenyl-pentadiene $(C_6H_5CH : CH)_2 : C : C(C_6H_5)_2$, sulphur-yellow crystals, m.p. 174°, from diphenyl-ketene and dibenzal-acetone (B. **41,** 1493).

Ketones.—1. The diolefin-ketones of this group are generally obtained by condensation of benzaldehydes (two molecules) with ketones (one molecule) which contain the group $—CH_2COCH_2—$:

$$2C_6H_5CHO+CH_3COCH_3=C_6H_5.CH : CHCOCH : CHC_6H_5+2H_2O.$$

Dibenzylidene-acetone, *dibenzal-acetone* $C_6H_5CH : CH.COCH : CHC_6H_5$, yellow needles, m.p. 112°; oxime, m.p. 143°, gives two isomeric hydroxylamine oximes $C_6H_5CH : CHC(NOH)CH_2.CH(NHOH)C_6H_5$, m.p. 165° and 201° (C. 1900, I. 336) by the reduction of a second molecule of hydroxylamine.

The dibenzyl-acetone gives with HCl not only the normal colourless addition products, but also a yellow unstable monochlorohydrate which in solution partly splits up into its components and unites with a second molecule HCl or metallic salts like ferric or mercuric chloride to intensely red double compounds (B. **37,** 3277, 3364).

By the action of acetic anhydride and concentrated sulphuric acid, dibenzal-acetone takes up water and is changed into **diphenyl-cyclopentenolone** $\begin{matrix}C_6H_5CH—CH_2\\ C_6H_5C=C(OH)\end{matrix}\!\!>\!CO$, m.p. 176° (B. **37,** 1133).

Dibenzal-acetone dichloride, *dicinnamenyl-dichloro-methane* $(C_6H_5CH : CH)_2CCl_2$, m.p. 77°, produced by the action of PCl_5 upon dibenzal-acetone in benzene solution, shows in its properties a far-reaching analogy with triphenyl-chloro-methane. It dissolves in concentrated sulphuric acid with a violet colour, and gives, with metallic salts like mercuric and stannic chloride, double compounds of the same colour. Its purple solution in SO_2 contacts the electric current. One of the two chlorine atoms is very lightly bound and can easily be exchanged for other groups like OH, OCH_3, etc. The **dicinnamenyl-chloro-carbinol** $(C_6H_5CH : CH)_2C(OH)Cl$, m.p. 56°, formed by treatment with moist silver oxide, is very stable and resembles triphenyl-carbinol. Like the latter, it dissolves with an intense colour in concentrated sulphuric acid. It is very easily esterified (methyl ether, m.p. 55°), and is easily converted by gaseous HCl into the dichloride, and by HBr into chloro-bromide in which the bromine atom shows the chief reaction. The reason for this property is to be found in the particularly strong valency binding by the cinnamenyl group, which surpasses that of the phenyl group, since in the benzo-phenone chloride $C_6H_5CCl_2C_6H_5$ no loosening of the chlorine atom is to be observed, whereas the dichloride of the benzylidene-aceto-phenone $C_6H_5CH : CH.CCl_2C_6H_5$ shows similar phenomena (B. **39,** 2977; **40,** 2689; A. **370,** 315).

Benzal-benzyl-acetone $C_6H_5CH : CHCOCH_2CH_2C_6H_5$, m.p. 53°, from benzaldehyde and benzyl-acetone with soda. Sodium amalgam reduces it to *dibenzyl-acetone* $(C_6H_5CH_2CH_2)_2CO$, b.p.$_{180}$ 280°–285° (A. **330,** 185). **p_2-Dinitro-dibenzyl-acetone,** see B. **37,** 1993.

o-Oxy-dibenzal-acetone, yellow flakes, m.p. 139° (B. **31,** 728).

o_2-Dioxy-dibenzal-acetone, *o-dicumarketone,* m.p. 160°, **p_2-dioxy-dibenzal-acetone,** m.p. 238°, orange-yellow crystals, the unstable modification consisting of dark-green flakes (B. **26,** 129). **Dibenzal-diethyl-ketone,** m.p. 122° (B. **31,** 1886).

Cinnamylidene-aceto-phenone $C_6H_5CH : CH.CH : CHCOC_6H_5$, m.p. 103°, from cinnamic aldehyde and aceto-phenone. Its oxime, m.p. 131°, is condensed by heating to $\alpha_1\alpha_1$-diphenyl-pyridin (B. **28,** 1730); homologues, see B. **35,** 1065.

Dibenzoyl-propane $CH_2(CH_2COC_6H_5)_2$, m.p. 67°, is formed from glutaryl-chloride-benzene and $AlCl_3$. Also by splitting up $\alpha_1\alpha_1$-dibenzoyl-glutaric ester obtained from benzoyl-acetic ester with CH_2I_2 or formaldehyde.

Dibenzoyl-diphenyl-propane $CH_2[CH(C_6H_5)COC_6H_5]_2$, m.p. 146°, from formaldehyde and desoxy-benzoïn. The reduction of its 1, 5-diketone produces cyclic pinacones of the pentamethylene group (B. **24,** R. 323; A. **302,** 215, 223).

1, 5-Diketones of this group are obtained by condensing benzaldehydes (one molecule) and aceto-phenones (two molecules) with sodium hydroxide: **benzylidene-diaceto-phenone** $C_6H_5CH(CH_2.CO.C_6H_5)_2$, m.p. 85°, and **o-oxy-benzylidene-diaceto-phenone** $(OH)[2]C_6H_4(CH_2.CO.C_6H_5)_2$, melting at 131°. By varying the conditions and condensing two molecules of benzaldehyde with three molecules of aceto-phenone, two isomeric **dibenzylidene-triaceto-phenones** $(C_6H_5CH)_2(CH_2COC_6H_5)_2$, melting at 198° and 256° respectively, are produced.

Benzamarone, *benzylidene-bis-desoxy-benzoïn* $C_6H_5COCH(C_6H_5)CH(C_6H_5).CH(C_6H_5)COC_6H_5$ (?), exists in two modifications, melting at 219° and 180°. It is prepared by condensing benzaldehyde with desoxy-benzoïn, as well as by the addition of desoxy-benzoïn to benzylidene-desoxy-benzoïn by the aid of sodium ethylate. Similarly, desoxy-benzoïn attaches itself to the unsaturated unions of other olefin derivatives—*e.g.* α-phenyl-cinnamo-nitrile, benzal-aceto-acetic ester, benzal-benzoyl-pyro-racemic ester, etc. (B. **25,** 1087). By decomposition with sodium ethylate, benzamarone yields the sodium salt of *amaric acid* $C_{23}H_{20}O_3$, and with sodium iso-butylate it forms *dimethyl-amaric acid* $C_{25}H_{26}O_3$ (A. **275,** 50).

The dry distillation of benzamarone produces desoxy-benzoïn, benzylidene-desoxy-benzoïn, and a body isomeric with the latter (B. **26,** 818). Hydroxylamine changes it quite readily into *pentaphenyl-pyridin.*

Carboxyl Derivatives of the ω, ω-Diphenyl-pentane Group.—**Styryl-phenacyl-propionic acid** $\begin{matrix}C_6H_5CH:CH\\C_6H_5CO.CH_2\end{matrix}\!\!>\!CHCH_2COOH$, m.p. 125°, from the condensation product of cinnamylidene-aceto-phenone with malonic ester by saponification and rejection of CO_2. On reduction it yields **phenacyl-succinic acid** $C_6H_5COCH_2CH(COOH).CH_2COOH$ (C. 1903, II. 944).

Diphenyl-acetic acid $(C_6H_5COCH_2)_2CHCO_2H$, m.p. 133°, from **diphenacyl-malonic ester** $(C_6H_5COCH_2)_2C(CO_2R)_2$ or **diphenacyl-aceto-acetic ester** $(C_6H_5COCH_2)_2C(COCH_3)COOC_2H_5$, m.p. 83°, the products of the action of phenacyl bromide upon malonic ester and aceto-acetic ester (B. **22,** 3225). It is also formed by alkaline condensation of aceto-phenone with glyoxylic acid, as well as the action of cold soda upon benzoyl-acrylic acid, wherein the latter splits up into aceto-phenone and glyoxylic acid (C. 1909, II. 125). Diphenacyl-acetic acid, being an ε-diketone, forms with ammonia a pyridin derivative (B. **29,** 798).

Dibenzyl-acetone-dicarboxylic ester $C_6H_5CH_2(CO_2R)COCH(CO_2R)CH_2C_6H_5$ is formed on benzylating acetone-dicarboxylic ester (Vol. I.), besides the monobenzylated and tribenzylated product (B. **34,** 1996).

Acetone-diphthalide $CO[CH_2\dot{C}HC_6H_4[2]C\dot{O}O]_2$, m.p. 137°, from phthal-aldehydic acid and acetone, besides acetonyl-monophthalide (C. 1898, II. 980).

Benzylidene-bis-benzoyl-acetic ester $C_6H_5CH[CH(CO_2R)COC_6H_5]2$ from benzal-benzoyl-acetic ester with benzoyl-acetic ester. It is easily split by alcoholic sodium ethylate into these components (B. **33,** 3183).

G. *ω, ω-Diphenyl-hexane Group and Higher Homologues.*—**1, 6-Diphenyl-hexadiene** $C_6H_5CH : CH.CH_2.CH_2.CH : CHC_6H_5$, m.p. 82°, is formed, besides an isomeric liquid hydrocarbon, by the action of Mg upon cinnamyl chloride $C_6H_5CH : CH.CH_2Cl$ (B. **43,** 172). **Tetraphenyl-hexatriene** $C_6H_5CH : CH.CH : CH.C(C_6H_5) : C(C_6H_5)_2$, yellow prisms, m.p. 159°, from diphenyl-ketone and cinnamylidene-acetophenone (B. **42,** 4249). **Hydro-cinnamoin** $C_6H_5CH : CH.CH(OH).CH(OH).CH : CHC_6H_5$, m.p. 154°, is obtained, besides other products, by the reduction of cinnamic aldehyde with copper zinc in alcohol (B. **32,** 1296). **Dibenzoyl-diphenyl-butadiene** $\begin{matrix}C_6H_5COCH : CC_6H_5\\C_6H_5COCH : CC_6H_5\end{matrix}$ (?), m.p. 192°, from benzile and aceto-phenone, can be converted by reduction into tetraphenyl-benzol and its derivatives (A. **302,** 195).

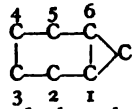
Oxalyl-diaceto-phenone $C_6H_5COCH_2COCOCH_2COC_6H_5$, m.p. 180°, is formed in the condensation of two molecules of aceto-phenone and oxalic ester with sodium alcoholate. Consult B. **28,** 1206, for the reduction-products of this tetraketone.

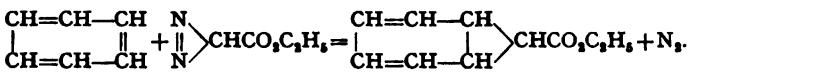
ω, ω-Diphenyl-diketo-hexane $(C_6H_5COCH_2CH_2)_2$. **Diphenyl-diketo-octane** $(C_6H_5COCH_2CH_2CH_2)_2$, and **diphenyl-diketo-nonane** $(C_6H_5CO.CH_2.CH_2.CH_2)_2CH_2$, are prepared from the chlorides of adipic acid, sebacic acid, and azelaic acid by means of benzene and aluminium chloride (B. **29,** R. 1157). **Cinnamylene-benzylidene-acetone** $C_6H_5CH : CH.CH : CH.COCH : CHC_6.H_5$, m.p. 106°, is derived from ω,ω-diphenyl-heptane. It is formed from cinnamylene-acetone and benzaldehyde (B. **29,** 615). *Cinnamylene-benzylidene-acetone* $C_6H_5CH : CH.CH : CH.COCH : CHC_6H_5$, m.p. 106°, is derived from ω, ω-diphenyl-heptane. It is formed from cinnamylene-acetone and benzaldehyde (B. **29,** 615). **Diphenyl-butadiene,** *diphenyl-octa-tetrene* $C_6H_5CH : CH.CH : CH.CH : CH.CH : CHC_6H_5$, m.p. 225° with decomposition, golden-yellow flakes, is formed besides **dicinnamylidene-succinic anhydride** $\begin{matrix}C_6H_5CH : CH.CH : CCO\\C_6H_5CH : CH.CH : \dot{C}CO\end{matrix}\rangle O$, m.p. 215°, brick-red needles, by condensation of cinnamic aldehyde with sodium succinate by acetic anhydride (A. **331,** 165). A stereo-isomeric (?) *white* diphenyl-octa-tetrene, m.p. 124°, is formed from cinnamic aldehyde, succinic ester, and sodium ethylate, besides other products (B. **34,** 2190). Illumination converts the yellow into the white hydrocarbon (B. **42,** 565).

B. Condensed Nuclei.

The condensed nuclei to be discussed in the following section are characterised by the fact that in them C atoms of the benzene nuclei participate in the formation of other carbocyclic rings.

Substances to which bicyclic formulæ are attributed have already been mentioned. Compare bicyclo-pentane, bicyclic ketone, carone, thujone, pinene, camphene, tricyclene, camphor, fenchone, etc. It should be noted that the capacity of forming bicyclic combinations in the hydro-aromatic substances is more varied than in the benzene derivatives proper, and is not confined to the 1, 2-position.

The bicyclic system of carone  , representing the condensed benzene-trimethylene ring, and whose hypothetical hydrogen compound is called **norcarane,** has been made accessible, in a more general synthetic manner, by heating diazo-acetic ester with benzene or its derivatives (Buchner, B. **33,** 3453 ; **34,** 982 ; **36,** 3502 ; **37,** 931) :



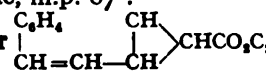
$\Delta^{2,4}$-Norcaradiene-7-carboxylic ethyl ester, *pseudo-phenyl-acetic ester,* followed by

$\Delta^{2,4}$-Norcaradiene-7-carboxylic ethyl ester, *pseudo-phenyl-acetic ester* $C_6H_6CHCO_2C_2H_5$, is formed from benzene and diazo-acetic ester by heating under pressure to 135°–140°. The raw ester, b.p.$_{18}$ 108°, partly converted into β-cyclo-heptatriene-carboxylic ester, gives, with concentrated sulphuric acid, a red colour passing into indigo blue. With ammonia we obtain the crystalline amide, m.p. 141°, which on saponification with sulphuric acid gives the oily, free acid. The latter with bromine gives a dibromide, m.p. 160° with decomposition, and a tetrabromide, m.p. 235° with decomposition. Oxidation with permanganate is complicated. It results in benzoic acid, o-, and p-phthalic acid, and trimethylene-tricarboxylic acid (splitting of the benzene ring). Heating under pressure transposes the ester into β-cyclo-heptatriene-carboxylic ester, while boiling the ester or amide with alkalies produces α-cyclo-heptatriene-carboxylic acid (splitting of the trimethylene ring between 1 and 6). Treatment with concentrated sulphuric acid transposes the amide into phenyl-acetamide $C_6H_5.CH_2CONH_2$ (splitting of the trimethylene ring between 1 and 7).

$\Delta^{2,4}$-3-Methyl-norcaradiene-carboxylic ester, *pseudo-tolyl-acetic ester* $CH_3.C_6H_5 : CHCO_2C_2H_5$, b.p.$_{12}$ 122°–126°, from toluol and diazo-acetic ester, amide, m.p. 131°, gives on boiling with 30 per cent. sulphuric acid, p-tolyl-acetic acid ; by prolonged shaking with ammonia, methyl-cyclo-heptatriene-carboxylic ester, m.p. 108°.

8, 5-Dimethyl-norcaradiene-carboxylic ester, *pseudo-xylyl-acetic ester* $(CH_3)_2C_6H_4 : CHCO_2C_2H_5$, b.p.$_{10}$ 125°–135°, from m-xylol and diazo-acetic ester, amide, m.p. 142°, gives, with sulphuric acid, 2, 4-dimethyl-phenyl-acetic acid (A. **258,** 1).

1, 7-Norcarane-dicarboxylic ester $CO_2C_2H_5.C_6H_9 : CHCO_2C_2H_5$, b.p.$_{18}$ 160°, from Δ^1-tetrahydro-benzoic ester with diazo-acetic ester ; the acid, m.p. 153°, gives an anhydride, m.p. 87°.

Benzo-norcaradiene-carboxylic ester  , b.p.$_{11}$

163°–164°, from naphthalene with diazo-acetic ester. Acid, m.p. 166°; amide, m.p. 217°. Oxidation produces **carboxy-phenyl-trimethylene-dicarboxylic acid** $CO_2H.C_6H_4CH\begin{matrix}\diagup\\\diagdown\end{matrix}CHCO_2H$, which has been further disintegrated to trimethylene-tricarboxylic acid. In this connection some substances should be mentioned which are derived from a condensed benzene and heptamethyl ring, **benzo-cyclo-heptane.**

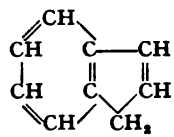
Benzo-cyclo-heptanone $C_6H_4\begin{cases}[1]CH_2.CH_2\\[2]CO.CH_2\end{cases}\!\!>CH_2$, b.p. 270°, is formed by condensation of Δ-phenyl-valeric acid chloride by means of $AlCl_3$; its oxime, m.p. 109°, gives on reduction benzo-α-amino-cyclo-heptane, whose chlorohydrate, on heating, decomposes into sal ammoniac and **benzo-cyclo-heptene** $C_6H_4\begin{cases}[1]CH_2—CH_2\\[2]CH=CH\end{cases}\!\!>CH_2$, b.p. 234°. The latter is split up by oxidation to o-phenylene-butyro-carboxylic acid (C. 1903, I. 586, 882).

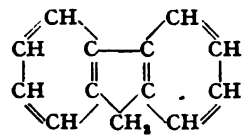
Benzo-cyclo-heptadione $C_6H_4\begin{cases}[1]CO.CH_2\\[2]CO.CH_2\end{cases}\!\!>H_2$, m.p. 46°, is formed by ketone-splitting of **phthalyl-glutaric esters** $C_6H_4\begin{cases}[1]CO.CH(CO_2R)\\[2]CO.CH(CO_2R)\end{cases}\!\!>CH_2$, obtained by condensation of phthalic ester and glutaric ester by means of sodium alcoholate (B. **32,** 2227).

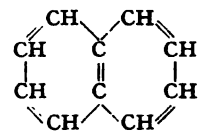
Benzo-cyclo-heptadienone $C_6H_4\begin{cases}[1]CH:CH\\[2]CH:CH\end{cases}\!\!>CO$, m.p. 67°, is formed from its dicarboxylic acid, m.p. 210°. The diethyl ester, m.p. 95°, is formed by condensation of o-phthal-aldehyde with acetone-dicarboxylic ester by means of diethylamine.

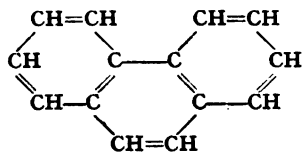
Homologues of benzo-cyclo-heptadienone are formed by the condensation of o-phthal-aldehyde with methyl-ethyl-ketone, diethyl-ketone, dibenzyl-ketone, etc., together with *acyl-hydrindones.* Sodium and alcohol reduce them to the corresponding benzo-cyclo-heptanols (A. **377,** 1).

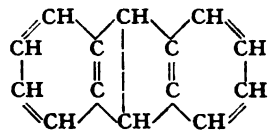
Of greater importance are the combinations of the benzene nuclei with five-membered nuclei, and of benzene nuclei with each other:


Indene


Fluorene


Naphthalene

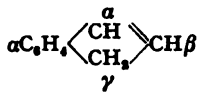

Phenanthrene


Anthracene.

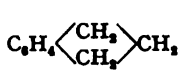
Although these condensed nuclei, as a rule, continue to manifest their aromatic character, they exhibit in their behaviour, in harmony with their peculiar structure, a series of wide differences from the true benzene compounds (see Naphthalene). They are eventually, by suitable oxidations, changed, like the homologues of benzene, into benzene-carboxylic acids. The parent hydrocarbons of these groups

occur, like benzene, chiefly in coal-tar, from which they are obtained in greater or lesser amount. Naphthalene is technically important; this is especially true of anthracene, the hydrocarbon of alizarin.

I. Indene and Hydrindene Group.



Indene

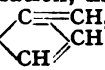
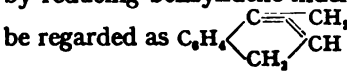
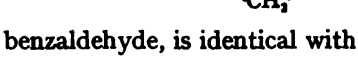


Hydrindene.

Indene has received its name from indol, because of its similarity to the latter in structure. By introducing NH into the methylene group of indene the formula of indol results.

Indene C_9H_8 is an oil, boiling at 178°; its specific gravity is 1·040 at 15°. It occurs, together with cumarone, to which it is very similar in its behaviour (B. **28,** 114), in that fraction of coal-tar boiling at 176°–182°, and can be extracted from it by means of its picric acid derivative (B. **28,** 3276). Very appreciable amounts of indene are also present in the condensation products resulting from the chilling of illuminating gas (B. **28,** 1331). It can also be obtained by the distillation of the calcium salt of synthetic hydrindene-carboxylic acid (B. **27,** R. 465).

It is best formed by heating α-hydrindamine chlorohydrate. Indene absorbs oxygen from the air and polymerises to indene resin on standing, heating, or treatment with concentrated sulphuric acid. It seems partly to be decomposed into *truxene* and hydrindene (B. **33,** 2257; **36,** 640). With chlorine and bromine it combines to form dichloro- and dibromo-hydrindene. It also forms *nitroso-chloride* and *nitrosite* like the terpenes (B. **28,** 1331). By treatment with sodium and alcohol, indene is reduced to hydrindene. At incandescent heat two molecules indene give up four H atoms to form chrysene.

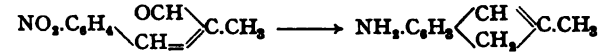
The hydrogen atoms of the CH_2 group in indene show a similar reactivity to those in cyclo-pentadiene. With oxalic ester it forms indene-oxalic ester, and with aldehydes, by alkaline condensation, intensely coloured hydrocarbons derived from benzo-fulvene  . Heating with halogen alkyl and caustic alkali produces mono- and di-alkylated indenes. It is remarkable that the benzyl-indene obtained by reducing benzylidene-indene with aluminium amalgam, which must be regarded as  on account of its condensation with benzaldehyde, is identical with the α-benzyl-indene  obtained by benzylating indene. There is therefore no isomerism between the α- and γ-alkyl-indenes (A. **347,** 249).

With benzaldehyde, indene combines to oxy-benzyl-indene, which partly passes into benzylidene-indene $C_9H_6 : CHC_6H_5$, m.p. 88°, yellow flakes, and partly combines with the second molecule of benzaldehyde to **oxy-benzyl-benzylidene-indene** $C_9H_5.CH(OH)C_6H_5(:CHC_6H_5)$, m.p. 135°, yellow crystals. **Cinnamylidene-indene** $C_9H_6 : CH.CH : CHC_6H_5$, m.p. 190°, yellowish-red needles.

Bz.-bromo-indene $C_6H_3Br(C_2H_4)$, b.p. 243°, is formed from hydrindene and bromine (B. **26,** 2251). It yields bromo-phthalic acid upon oxidation.

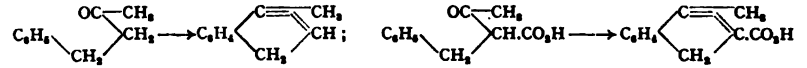
Indene derivatives are obtained synthetically by the following methods, which to some extent recall the syntheses of the pentamethylene compounds:

1. Benzene compounds, having the group $C_6H_5.C.C.CO$, split off water and condense to indene derivatives: (*a*) Nitro-α-alkyl-cinnamic aldehydes yield amido-β-alkyl-indenes (B. **22,** 1830):



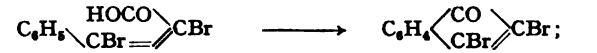
Nitro-α-methyl-cinnamo-aldehyde Amido-β-methyl-indene.

Similarly, benzyl-acetone and benzyl-aceto-acetic ester yield γ-methyl-indene and γ-methyl-indene-β-carboxylic acid (B. **20,** 1574; A. **247,** 157) when they are heated with sulphuric acid:

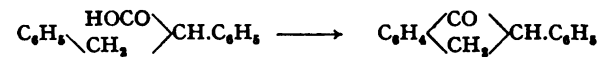


Benzyl-acetone γ-Methyl-indene Benzyl-acetic acid Methyl-indene-carboxylic acid.

(*b*) Substituted cinnamic acids yield *indone* derivatives when they are treated with hot sulphuric acid, just as the hydro-cinnamic acids, alkylised in the nucleus and in the side chain, yield *dihydro-indones.* Cinnamic and hydro-cinnamic acids themselves react with as little readiness as cinnamic aldehyde (A. **247,** 140; B. **25,** 2095, 2129):

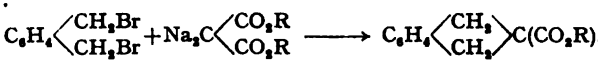


Dibromo-cinnamic acid Dibromo-indone.

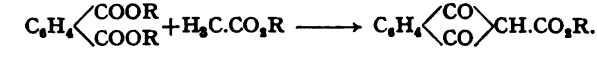


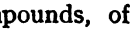
α-Phenyl-hydro-cinnamic acid β-Phenyl-hydrindone.

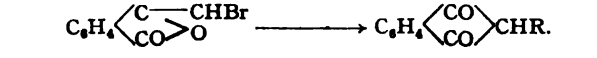
2. The *hydrindene* derivatives have been obtained in the same manner as the tetra- and pentamethylene derivatives: by the action of xylylene halides upon malonic ester and sodium alcoholate (B. **17,** 125; **18,** 378):



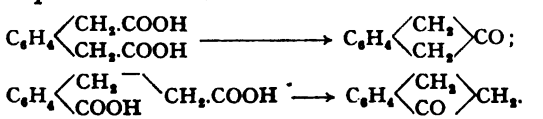
3*a*. The formation of αγ-diketo-hydrindenes from p-phthalic esters and fatty-acid esters or ketones (A. **252,** 72; B. **27,** R. 104, R. 19) corresponds to the condensation of oxalic esters to pentamethylene derivatives:



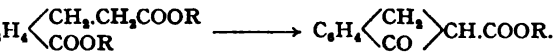
3*b*. The phthalide compounds, of the formula  , formed from phthalic anhydride and fatty acids, are transposed by sodium alcoholates into the sodium derivatives of the isomeric diketo-hydrindenes (B. **26,** 954, 2576):



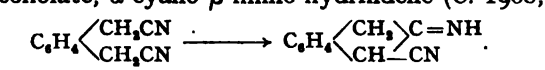
4a. The formation of dihydrindones by the distillation of salts of o-phenylene-diacetic acid and o-hydro-cinnamic acid (B. **26,** 222, R. 708) corresponds to the cyclic ketone formation of dicarboxylic acids of the adipic acid series :



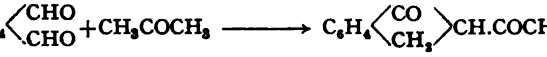
4b. Corresponding to the cyclic aceto-acetic ester condensation (p. 5), we have the formation of hydrindone-carboxylic esters by the action of Na or Na alcoholate upon the esters of o-phenylene-diacetic acid or o-hydro-cinnamo-carboxylic acid :



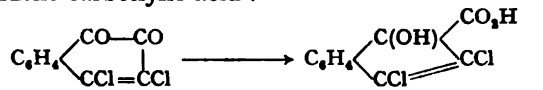
Similarly, we obtain from the o-phenylene-diaceto-nitrile, by means of sodium alcoholate, *α*-cyano-*β*-imino-hydrindene (C. 1908, I. 1274) :



5. Hydrindone derivatives are formed by alkaline condensation from o-phthal-aldehyde with methyl-ketones and methyl-ketone-carboxylic acids (A. **347,** 112 ; **369,** 287) :



6. The formation of indene derivatives from naphthalene derivatives is rather remarkable ; a six-membered benzene ring is rearranged to a ring of five members—similar to the production of pentamethylene derivatives from the benzenes, or fluorene compounds from phenanthraquinone. This change occurs by the action of chlorine or hypochlorous acid upon the naphthols, naphtho-quinones, amido-naphthols, etc. The first product consists of naphthalene keto-derivatives with the groups —CO.CO— or CO.CCl_2— ; these sustain the decomposition (B. **20,** 2890 ; **21,** 2719). Thus, dichloro-*β*-naphtho-quinone yields dichloroxy-indene-carboxylic acid :



Dichloro-*β*-naphtho-quinone Dichloroxy-indene-carboxylic acid.

Indene Derivatives.—*γ* (*α*)-**Methyl-indene** $C_6H_4 : C_3H_3.CH_3$, b.p. 206°, is formed by methylating indene, and, synthetically, from benzyl-acetone, also from its carboxylic acid by splitting off CO_2. *γ* (*α*)-**Benzyl-indene** $C_6H_4 : C_3H_3.CH_2C_6H_5$, b.p.$_{13}$ 184°. *α*, *γ*-**Dibenzyl-indene** $C_6H_4 : C_3H_2(CH_2C_6H_5)_2$, m.p. 63°, by benzylating indene, also by reduction of benzyl-benzylidene-indene, m.p. 137°, with aluminium amalgam (A. **347,** 262). **1, 2, 3-Triphenyl-indene,** m.p. 135° (C. 1908, II. 1736). **1, 1, 3-Triphenyl-indene,** m.p. 135° (B. **39,** 1030). **Bz.-amido-***β***-methyl-, -ethyl-, -iso-propyl-indene,** m.p. 98°, 89°, 84°.

β-**Nitro-indene** $C_6H_4 : C_3H_3NO_2$, m.p. 141°, yellow crystals, from indene nitrosite by distillation with water vapour. Zinc dust and glacial acetic acid reduce it to *β*-hydrindone-oxime (A. **336,** 1).

β-Indene-carboxylic acid $C_6H_4C_3H_3COOH$, m.p. 222°–230°, from hydrindene-carboxylic acid with bromine. **γ-Methyl-β-indene-carboxylic acid,** m.p. 200°, from benzyl-aceto-acetic ester.

Indene-oxalic ethyl ester $C_6H_4 : C_3H_3.COCOOC_2H_5$, m.p. 87°, orange-red needles, from indene-oxalic ester and sodium ethylate, gives, on reduction with aluminium amalgam, **indene-oxy-acetic ester** $C_6H_4 : C_3H_3.CH(OH)CO_2C_2H_5$, b.p.$_{13}$ 172°, which, by saponification and loss of water, gives **benzo-fulvene-carboxylic acid** $C_6H_4 : C_3H_2 : CHCO_2H$, decomposing at 175°, orange flakes. The latter, on reduction, yields **indene-acetic acid** $C_6H_4 : C_3H_3.CH_2CO_2H$, m.p. 96°, which, on further condensation, passes into **benzo-fulvene-carboxylic acetic acid** $C_6H_4 : C_3H(: CHCO_2H)CH_2CO_2H$, m.p. 245° with decomposition (A. **347,** 275).

β, γ-Dichloro-α-oxy-indene-carboxylic acid, melting at 100°, is obtained from β-dichloro-naphtho-quinone. Chromic acid oxidises it to dichlorindone. It is changed to chlorindone-carboxylic acid when digested with concentrated sulphuric acid (B. **28,** R. 279).

α, β-Diphenyl-indone $C_6H_4\langle^{C(C_6H_5)}_{CO}\rangle C(C_6H_5)$, garnet-red crystals, melting at 151°, is produced, together with triphenyl-acrylic acid, when benzo-phenone chloride is condensed with phenyl-acetic ester. It yields triphenyl-propane upon reduction. It is decomposed into α, β-diphenyl-vinyl-o-benzoic acid when fused with caustic potash. It can be recovered from this as well as from triphenyl-acrylic acid on heating with zinc chloride (B. **30,** 1281).

β-Phenyl-o-, m-, and **p-nitro-indone** $NO_2C_6H_3\langle^{CH}_{CO}\rangle C(C_6H_5)$, m.p. 139°, 205°, and 215°–217°, from o-, m-, and p-nitro-phenyl-α-phenyl-cinnamic acid (C. 1900, II. 1276).

Indone-β-acetic acid $C_6H_4\langle^{CH}_{CO}\rangle C.CH_2CO_2H$, m.p. 99°, from phenyl-itaconic acid with concentrated sulphuric acid, lemon-yellow prisms. It is isomerised, by prolonged action of mineral acids, to saturated colourless lactone, m.p. 123° (B. **41,** 3983). Similarly we obtain **γ-methyl-γ-phenyl-indone-β-acetic acid** and **γ-phenyl-indone-β-propionic acid,** m.p. 155°, 167°, and 168° respectively, from methyl-phenyl-itaconic acid, diphenyl-itaconic acid, and α-methyl-γγ-diphenyl-itaconic acid.

γ-Bromindone $C_6H_4 : C_3BrHO$, m.p. 64°, **β, γ-dichloro-** and **dibromo-indone** $C_6H_4 : C_3Br_2O$, m.p. 90° and 123°, are obtained synthetically from monobromo-dichloro- and dibromo-cinnamic acid (B. **32,** 2477; **33,** 2426). The β-halogen atom is easily replaced by OH and NHR: **β-chloro-** and **β-bromo-γ-oxy-indone,** m.p. 114° and 119°; **γ-anilido-indone,** m.p. 105° with decomposition, is converted into diketo-hydrindene by HCl. A halogen atom also easily reacts with Na-malonic and acetic esters, etc., the resulting substances being feebly yellow, but giving fine purple colours with alkalies, resembling cochineal (B. **31,** 2079, 2903; **33,** 2418, 2425; **35,** 2938).

Perchlorindone $C_6Cl_4 : C_3Cl_2O$, m.p. 149°, from a monocyclic pentene derivative, hexachloroxy-cyclo-pentene-carboxylic acid, produced by the splitting of hexachloro-diketo-cyclo-hexene, by warming with water, or sodium acetate solution (A. **367,** 1).

Hydrindene Derivatives.—**Hydrindene** $C_6H_4 : C_3H_6$ is an oil, boiling at 177°. It results when indene is reduced with sodium and alcohol. For other methods, see B. **33,** 735 ; **34,** 1247 ; C. 1903, II. 989.

Dichloro-hydrindene is an oil. **Dibromo-hydrindene** $C_6H_4 : C_3H_4Br_2$ melts at 44°. They yield **chlor-** and **bromoxy-hydrindenes,** melting at 129° and 131°, when digested with water. Ammonia converts the latter bodies, in the cold, into **amido-oxy-hydrindene,** melting at 133°, which nitrous acid transposes into *β, γ*-**dioxy-hydrindene,** *hydrindene-glycol* $C_6H_4 : C_3H_4(OH)_2$, melting at 99° (B. **26,** 1539 ; **32,** 30).

Hydrindene-β-carboxylic acid $C_6H_4(CH_2)_2CH.CO_2H$, melting at 130°, is converted by distillation of its salts into indene, by bromine into indene-carboxylic acid, and is oxidised by $KMnO_4$ to o-carbo-phenyl-glyoxylic acid. It results when CO_2 is eliminated from **hydrindene-β-dicarboxylic acid,** melting at 199°. The ester of the latter acid may be obtained synthetically from xylylene bromide and malonic ester.

β-Aceto-hydrindene-carboxylic ester $C_6H_4(CH_2)_2C\begin{matrix}COCH_3\\CO_2R\end{matrix}$ is obtained from xylylene bromide and aceto-acetic ester.

γ-Methyl-hydrindene-β-carboxylic acid, m.p. 86° ; see C. 1906, I. 1699.

Hydrindene-β-methyl-, ethyl-, and **phenyl-ketones** are formed in the distillation of hydrindene-carboxylic acid with benzoic acid, propionic acid, and acetic acid (B. **26,** 1539).

α-Hydrindone, α-indanone $C_6H_4\begin{matrix}CH_2\\CO\end{matrix}>CH_2$, melting at 41° and boiling at 244°, is obtained in the dry distillation of o-carbohydro-cinnamic acid as well as from o-cyan-hydro-cinnamic ester upon digesting with concentrated hydrochloric acid. The *phenyl-hydrazone* melts at 131°. The *oxime,* melting at 146°, is changed, by reduction, to *α-amido-hydrindene,* **hydrindamine,** melting at 220°.

The chlorohydrate decomposes almost quantitatively into AmCl and indene, on heating.

N_2O_3 converts it into *α-oxy-hydrindene,* melting at 54° (B. **26,** R. 708). Phosphorus pentachloride converts α-hydrindone-oxime into hydro-carbo-styril (Beckmann's transposition) (B. **27,** R. 598) :

$$C_6H_4\begin{matrix}CH_2-\\C(NOH)\end{matrix}>CH_2 \longrightarrow C_6H_4\begin{matrix}CH_2-CH_2\\NH-CO\end{matrix}.$$

Hydrindone-azine $C_9H_8 : N.N : C_9H_8$, melting at 165°, results from the action of hydrazin upon the oxime. Nitrous acid converts hydrindone into **iso-nitroso-hydrindone** $C_6H_4\begin{matrix}CH_2\\CO\end{matrix}>C=NOH$, melting with decomposition at 210°. This phenyl-hydrazin changes to a *osazone,* melting at 229°. The latter is isomeric with the dihydrazone obtained from *α, γ*-diketo-hydrindene. It yields **β-amido-α-hydrindone** when it is reduced (B. **29,** 2605, R. 869 ; C. 1897, I. 860).

Concentrated H_2SO_4 produces Beckmann's transposition, and forms homo-phthalamidic acid (C. 1907, I. 727). With benzaldehyde (B. **34,** 412) α-hydrindene gives a benzylidene compound $C_9H_8O : CHC_6H_5$, yellow crystals, m.p. 114°, also yielded by α-benzyl-cinnamic acid, with concentrated sulphuric acid ; two molecules hydrindone condense to

anhydro-bis-hydrindone $C_9H_6O : C_9H_8$, m.p. 143°, which, on further condensation, gives the hydrocarbon *truxene* $(C_9H_6)_x$ (C. 1894, II. 92; B. **31**, 720; **33**, 3085; **36**, 645). With o-phthal-aldehyde α-hydrindone condenses to **iso-naphtho-fluorenone** $\begin{matrix}C_6H_4\\ \\ C_{10}H_6\end{matrix}\!\!>\!CO$ (A. **369**, 288).

When o-, m-, and p-methyl-hydro-cinnamic acids are heated they yield **o-, m-,** and **p-methyl-α-hydrindones.** The constitution of the latter is deduced from their oxidation to the various methyl-o-phthalic acids. **Bz.-Chloro-, bromo-, iodo-,** and **nitro-hydrindones** behave similarly (B. **25**, 2095).

β-Methyl-α-hydrindone, melting at 168° (11 mm.), and **β-phenyl-α-hydrindone,** melting at 78°, are obtained from α-methyl- and phenyl-hydro-cinnamic acids. When its ethereal solution is shaken with caustic soda β-phenyl-hydrindone is changed partly to **β-phenyl-oxy-hydrindone,** melting at 129°, and in part by rupture of the ring into desoxy-benzoïn-o-carboxylic acid $C_6H_4(CO.OH).CH_2.COC_6H_5$ (B. **26**, 2095). **γ-Phenyl-α-hydrindone,** melting at 78°, is prepared from β, β-diphenyl-propionic acid (B. **26**, 2128).

ββ-Dimethyl-α-hydrindone $C_6H_4\langle\begin{matrix}CH_2\\ CO\end{matrix}\rangle C(CH_3)_2$, m.p. 45°, from αα-dimethyl-β-phenyl-propionic acid chloride and $AlCl_3$, or by methylation of α-hydrindone by means of $NaNH_2$ and CH_3I. On heating with $NaNH_2$ in benzene solution, it is split into the amide of αα-dimethyl-β-phenyl-propionic acid. **ββ-Diethyl-α-hydrindone,** m.p. 7°, b.p.$_{18}$ 138° (C. 1910, II. 39).

Tetrachloro-α-hydrindone $C_6H_4 : C_3Cl_4O$, melting at 108°, is the addition product of chlorine and dichlorindone. It is readily decomposed by digestion with alcoholic sodium hydrate into o-trichloro-vinyl-benzoic acid. **Chloro-dibromo-hydrindone-γ-carboxylic acid** $C_6H_4 : [C_3ClBr_2O(COOH)]$, melting at 171°, is made from chlorindone-γ-carboxylic acid and bromine. It is similarly decomposed into bromo-chloro-methylene-homo-phthalic acid.

β-Nitro-α-hydrindone $C_6H_4\langle\begin{matrix}CH_2\\ CO\end{matrix}\rangle CH.NO_2$, sulphur-yellow needles, m.p. 117° with decomposition, is formed by condensation of o-phthal-aldehyde with nitro-methane and sodium ethylate (A. **377**, 15).

β-Hydrindone, *β-indanone* $C_6H_4(CH_2)_2CO$, m.p. 61°, b.p. 220°–225° with decomposition, is formed by the distillation of calcium o-phenylene diacetate, and by heating hydrindene-glycol, or its monomethyl ether, with sulphuric acid. Hydrazone, m.p. 120°. Oxime, m.p. 155°, gives, by reduction, **β-amido-hydrindene** (B. **26**, R. 709). **Di-iso-nitroso-β-hydrindone** $C_6H_4[C(NOH)]_2CO_2$, m.p. 233° with decomposition. Like the α-hydrindone and the diketo-hydrindene, the β-hydrindone easily condenses to anhydro-bis-β-hydrindone $C_9H_6O : C_9H_8$, m.p. 170° (B. **32**, 28).

Tetrachloro-β-hydrindone $C_6H_4 : C_3Cl_4O$, m.p. 98°, is formed by the action of bleaching-lime upon tetrachloro-2, 3-diketo-tetrahydro-naphthalin. **Monobromo-, α, γ-dibromo-,** and **tetrabromo-hydrindone,** m.p. 91°, 111°, and 173°, by bromination of β-hydrindone in benzene solution. Tetrachloro- and tetrabromo-hydrindone on heating with alkalies pass into phthalide-carboxylic acid (benzilic acid transposition) (A. **334**, 346; C. 1908, II. 1183).

β-Acetyl- and **β-benzoyl-α-hydrindone,** m.p. 76° and 98° (A. **347,** 112); **α-hydrindone-β-oxalic acid,** m.p. 212° (A. **369,** 287).

α,γ-Diketo-hydrindene $C_6H_4(CO)_2CH_2$, melting with decomposition at 130°, is obtained from its carboxylic acid (below). It consists of colourless needles, which dissolve readily with a yellow colour in alkalies. The hydrogen atoms of the methylene groups placed between the two keto-groups have an acid nature. Phenyl-hydrazin converts it into a *monohydrazone,* melting at 163°, and a *dihydrazone* $C_6H_4(C:NNHC_6H_5)_2CH_2$, melting at 171°. Diazo-benzene chloride converts the monohydrazone into a *triketo-hydrindene* $C_6H_4(CO)_2C:NNHC_6H_5$, which is also prepared by the decomposition of *benzal-diketo-hydrindene* $C_6H_4(CO)_2C=CHC_6H_5$, a condensation product of benzaldehyde and diketo-hydrindene, with phenyl-hydrazin.

8, 4-Dioxy-benzal-diketo-hydrindene, melting at 257°, and prepared by the condensation of proto-catechuic aldehyde and diketo-hydrindene, is a dye (B. **30,** 1185).

With p-amido-benzaldehydes, also, feebly basic dyes are obtained. o-Amido-benzaldehyde yields the so-called **quinolene-phenylene-ketone** $C_6H_4\left\{\begin{matrix}[1]CH=C-\\ [2]N-\dot{C}.CO\end{matrix}\right\}C_6H_4$, m.p. 175° (B. **34,** 2467).

With orthoformic ester, indane-dione condenses to the compounds $C_6H_4(CO)_2C:CHOH$ and $C_6H_4(CO_2)C:CH.CH(CO_2)C_6H$. With ammonia we obtain from this **dibenzoylene-pyridin** $\begin{matrix}CO-C.CH:C-CO\\ C_6H_4.\dot{C}.N:\dot{C}-C_6H_4\end{matrix}$ (C. 1903, II. 950). With ethoxy-methylene-aceto-acetic ester (Vol. I.), indane-dione forms **indane-dione-methenyl-aceto-acetic ester,** m.p. 118°, which is condensed by concentrated alkali to **8-oxy-diphenylene-ketone-2-carboxylic acid** (C. 1906, I. 849). By heating diketo-hydrindene by itself or boiling with water, **anhydro-bis-diketo-hydrindene-*bindone*** $C_6H_4(CO)_2C=C\begin{matrix}C_6H_4\\ CH_2\end{matrix}>CO$ is formed, yielding intensely coloured metallic compounds. Heated with aromatic amines, it gives, like cœrulignone, beautiful blue dyes (B. **30,** 3137). Phenyl-hydrazin splits it into two molecules diketo-hydrindene-dihydrazone (A. **277,** 362; B. **34,** 3269). The anhydro-bis-diketo-hydrindene can undergo higher condensation (B. **31,** 2935; **33,** 2433).

β-Methyl-diketo-hydrindene $C_6H_4(CO)_2CHCH_3$, m.p. 85°, is formed from its carboxylic acid. Its sodium compound gives, with methyl iodide, **β-dimethyl-diketo-hydrindene** $C_6H_4(CO_2)C(CH_3)_2$. **β-Phenyl-diketo-hydrindene,** m.p. 145°, from benzal-phthalide. The *isatin-diphthalyl,* m.p. above 350°, violet needles, similarly obtained by transposition of ethine-diphthalyl, is now regarded as derived from a hydrocarbon, naphthacene $C_{18}H_{12}$ compound of two naphthalene nuclei, and has the structure $C_6H_4\begin{matrix}C(OH):C.CO\\ C(OH):\dot{C}.CO\end{matrix}>C_6H_4$ (B. **31,** 1272). **β, β-Diethyl-diketo-hydrindone** $C_6H_4(CO)_2C(C_2H_5)_2$, b.p.$_{10}$ 143°–156°, oxime, m.p. 143°, from benzene, diethyl-malonyl chloride, and $AlCl_3$ (A. **373,** 291).

β-Dichloro-diketo-hydrindene $C_6H_4(CO)_2CCl_2$, m.p. 125°, by the action of chlorine upon γ-oxy-chlorindone. It is split up into o-phthalic acid by dilute soda (B. **21,** 491, 2380).

β-Bromo-diketo-hydrindene $C_6H_4(CO)_2CHBr$ is identical with β-bromo-γ-oxy-indone and is formed also from diketo-hydrindene-carboxylic ester by bromination and saponification. Boiling with water

gives **dibromo-diketo-hydrindene** $C_6H_4(CO)_2CBr_2$ and finally **tris-diketo-hydrindene** $C_6H_4(CO)_2C[CH(CO)_2C_6H_4]_2$; see also B. **33**, 2433; **34**, 2145.

Diketo-hydrindene-carboxylic ester $C_6H_4(CO)_2CH.COOR$, m.p. 75°–78°, from phthalic ester with acetic ester and Na alcoholate, is easily converted into diketo-hydrindene. Other derivatives, see B. **31**, 2084; M. **31**, 62.

β-Acetyl and **β-benzoyl-diketo-hydrindene** $C_6H_4(CO)_2CH.COR$, m.p. 110° and 108°, from phthalic ester with acetone and aceto-phenone. Easily split up by alkalies (B. **27**, 104).

Indacene is the name of a tricyclic combination of a benzene nucleus with two cyclo-pentene nuclei. From m-xylylene-diaceto-acetic ester, with 80 per cent. H_2SO_4, we obtain dimethyl-indacene-carboxylic acid $CO_2HC\langle\begin{smallmatrix}C(CH_3)\\CH_2\end{smallmatrix}\rangle C_6H_2\langle\begin{smallmatrix}C(CH_3)\\CH_2\end{smallmatrix}\rangle CCO_2H$; from pyro-mellithic ester, acetic ester, and Na tetraketo-hydrindacene-dicarboxylic ester $CO_2RCH(CO)_2C_6H_2.(CO)_2CHCOOR$ (B. **34**, 2779).

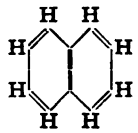
Fluorene is a *dibenzo-pentene* resulting from the union of the pentene nucleus with two benzene nuclei. It will be considered in conjunction with *chrysene-fluorene* and *picene-fluorene* after the condensed nuclei of the phenanthrene group—phenanthrene, chrysene, and picene,—to which the two first-named bodies are intimately related.

II. Naphthalene Group.

Garden (1816) discovered naphthalene $C_{10}H_8$, among the distillation products of coal-tar. It shows great similarity to benzene, from which it differs in constitution by C_4H_2. Like benzene, it is produced by the action of intense heat upon various carbon compounds; hence its occurrence in coal-tar. Numerous derivatives are obtained from it by the replacement of its hydrogen atoms; they are very similar to the benzene compounds. Only the most important of them will be considered in the following sections.

Constitution of the Naphthalene Nucleus.

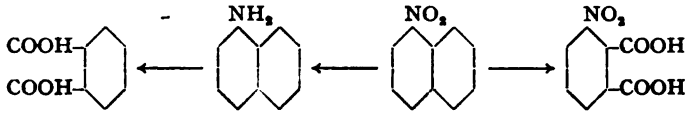
The behaviour of naphthalene is satisfactorily explained by the formula first suggested by Erlenmeyer, sen. (A. **137**, 346):



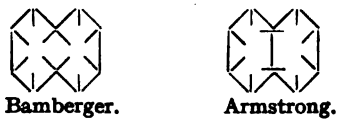
It consists of two benzene nuclei, having in common two carbon atoms occupying the ortho-position. Graebe (1866) proved the correctness of the formula (A. **149**, 20).

The oxidation of napthalene to o-phthalic acid shows the presence of a benzene nucleus. Further, the oxidation of dichloro-naphthoquinone $C_6H_4 : C_4Cl_2O_2$ also yields o-phthalic acid. If, however, dichloro-naptho-quinone is converted by PCl_5 into tetrachloro-naphthalene, this, upon oxidation, will become tetrachlor-o-phthalic acid. In the second instance, therefore, the benzene nucleus, which in the first case was unattacked, is now oxidised. A precisely similar method of de-

monstration, to which reference has already been made, is as follows : Nitro-naphthalene, obtained by nitration of naphthalene, yields nitro-o-phthalic acid ; whereas amido-naphthalene, resulting from the reduction of the preceding nitro-naphthalene, yields o-phthalic acid :

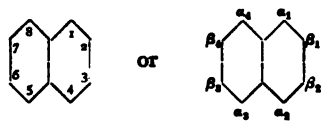


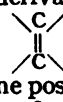
Hence it follows that naphthalene must consist of two symmetrically condensed benzene nuclei. For other formulæ, like the *central formula* of Bamberger, the formula of Armstrong, etc., consult B. **23**, R. 337, 692 ; **24**, R. 651, 728 :



Bamberger. Armstrong.

Isomerisms of the Naphthalene Derivatives.—The isomerisms of the derivatives of naphthalene conditioned by this formula agree with the facts. The substituents are designated according to the diagram :

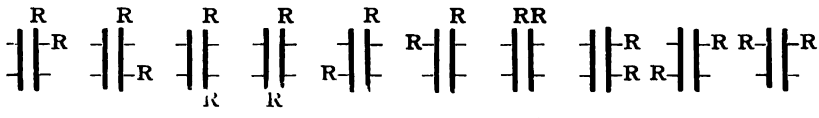


The replacement of an H atom in naphthalene can give rise to two isomeric mono-derivatives, distinguished as α- and β-derivatives according as the substituent is adjacent to the complex  common to both groups, or separated from it by a CH group. The positions 1, 4, 5, 8 (α_1, α_2, α_3, α_4) on the one side, and 2, 3, 6, 7 (β_1, β_2, β_3, β_4) are equivalent. Liebermann (A. **183**, 254) and Atterberg (B. **9**, 1736) have adduced proof of the equivalence of the four α-positions. The method adopted is similar to that followed in demonstrating the equal value of the benzene hydrogen atoms.

Whether a substituent occupies the α- or β-position is mainly determined by its oxidation to a corresponding o-phthalic acid derivative. Thus, if [1, 2, 3]-nitro-phthalic acid is obtained from α-nitro-phthalene, the nitro-group must consequently be adjacent to the contact position of the second benzene nucleus in naphthalene. The constitution of α-oxy-naphthalene or α-naphthol is evident also from its synthesis by means of phenyl-iso-crotonic acid $C_6H_5.CH : CH.CH_2.COOH$. Besides, only α-derivatives of naphthalene can be converted into quinones analogous to p-benzo-quinone, as these alone possess a free H atom in para-position with reference to the substituent. This latter circumstance also determines still other peculiarities in the behaviour of the compounds of naphthalene—*e.g.* the power of the naphthols and naphthylamines to unite with diazo-bodies, etc.

The di-substitution products of naphthalene, when the substituents are similar, can exist in ten isomeric forms, which are designated by numbers or prepositions (B. **26**, R. 533). In the following diagram the

double hexagon of naphthalin is replaced by two parallel lines, as was similarly done with benzene :



1,2 Ortho- 1,3 Meta- 1,4 Para- 1,5 Ana- 1,6 Epi- 1,7 Kata- 1,8 Peri- 2,3 2,6 Amphi- 2,7 Pros-

On the calculation of the isomeric possibilities of the naphthalin derivatives, see B. **33**, 2131.

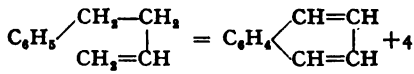
The position of the substituents in the di-derivatives can very often be determined by the oxidation method, if thereby it can first be ascertained whether the substituents are in the same nucleus (*isonuclear*) or in different nuclei (*heteronuclear*). Isonuclear substitution products with adjacent substituents, show in general the same behaviour as the ortho-substitution products of benzene, inasmuch as they form similar condensation products. However, a difference appears to exist between positions like 1, 2 and 2, 3. Thus, only those amido-naphthalenes manifest the ability to form naphtho-quinolin rings, in which the pyridene ring can attach itself to α, β- C atoms. It must be assumed that the double linkages in naphthalene are not so easily displaced as in benzene. The behaviour of the 1, 8- or peri-derivatives is remarkable. Like the o-di-derivatives, they exhibit a series of hetero-ring formations.

Naphthalene-ring Formations.

Naphthalene is produced by pyrogenic condensation from a series of carbon compounds, like *ethylene, acetylene, ether*, etc. Methods of producing the naphthalene nucleus by processes in which *one* benzene nucleus pre-exists are more important :

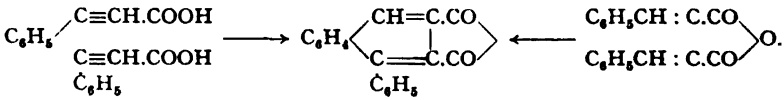
1. A mixture of *benzene* and *acetylene* conducted through a tube heated to redness yields naphthalene (*Bull.* **7**, 306).

2. It is derived from phenyl-butylene $C_6H_5.CH_2.CH_2.CH : CH_2$ and its dibromide, on leading their vapours over heated lime :

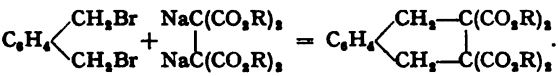


Similar reactions result in the formation of phenyl-dihydro-naphthoic acid from *dibenzal-propionic acid* with glacial acetic-sulphuric acid ; of *phenyl-bromo-tetrahydro-naphthoic acid* from benzyl-phenyl-isocrotonic acid with Br ; and of 1-*phenyl-tribromo-naphthalene* by the bromination of diphenyl-diacetylene (A. **341**, 198).

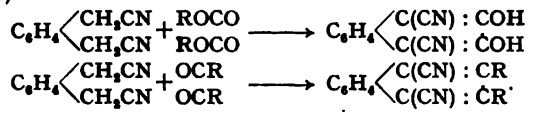
3. *Phenyl-propiolic acid*, on heating with acetic anhydride or treating with $POCl_3$, passes into the anhydride, while phenyl-propiolic ester, on heating to 200°, forms the ester of 1-*phenyl-naphthalene*-2, 3-*dicarboxylic acid*. This anhydride is also formed by illumination of dibenzal-succinic anhydride in benzene solution :



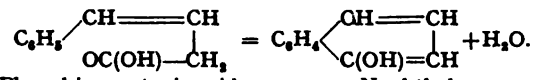
4. *Xylylene bromide* and *sodium-acetylene-tetracarboxylic ester* produce tetrahydro-naphthalene-tetracarboxylic ester, which, on saponification, yields tetrahydro-naphthalene-dicarboxylic acid, whose silver salt passes by distillation into naphthalene (Baeyer and Perkin, B. **17,** 488 ; cp. formation of the tetramethylene and indene rings) :



5. *o-Xylylene cyanide* condenses in the presence of Na ethylate with oxalic ester and α-diketones to form naphthalene derivatives (B. **43,** 1300) :

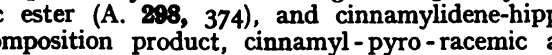


6. What is further noteworthy is the formation of α-naphthol from phenyl-iso-crotonic acid when heated (Fittig and Erdmann, B. **16,** 43 ; A. **247,** 372 ; **255,** 263 ; **275,** 284 ; cp. formation of indene derivatives) :

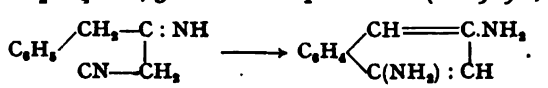


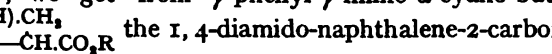
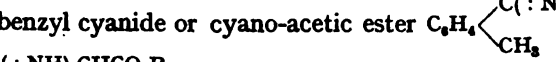
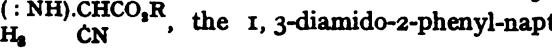
Phenyl-iso-crotonic acid α-Naphthol.

In a perfectly similar manner 5-, 6-, and *7-chloro-1-naphthols* are obtained from *o-, m-,* and *p-chloro-phenyl-paraconic acids*; 2- and 4-*methyl-naphthols* from α- and *β-methyl-paraconic acids*; α-naphthol-3-methyl-ketone (B. **26,** 345) from *β-benzal-lævulinic acid* and 2-phenyl-1, 3-dioxy-naphthalene is produced when α, γ-diphenyl-aceto-acetic ester is digested with concentrated sulphuric acid (A. **296,** 14).

Similarly, phenacetyl-malonic ester gives 1, 3-dioxy-naphthalene-2-carboxylic ester (A. **298,** 374), and cinnamylidene-hippuric acid, or its decomposition product, cinnamyl-pyro-racemic acid, gives  α-naphthoic acid (B. **85,** 384).

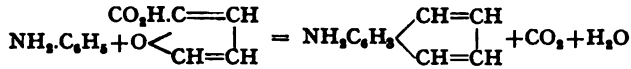
7. *γ-Phenyl-β-imino-butyro-nitrile* condenses under the action of concentrated H_2SO_4 to 1, 3-diamido-naphthalene (C. 1909 I, 857) :



Similarly, we get from γ-phenyl-γ-imino-α-cyano-butyric ester  the 1, 4-diamido-naphthalene-2-carboxylic ester, and, from the imino-nitriles obtained by the condensation of o-tolunitrile with benzyl cyanide or cyano-acetic ester  and  , the 1, 3-diamido-2-phenyl-napthalin and

1, 3-diamido-naphthalin-2-carboxylic ester respectively (C. 1907, I. 728; II. 68, 539, 2053).

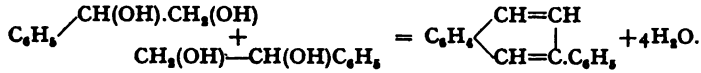
8. An interesting formation of α-naphthylamine consists in heating *aniline* with *pyro-mucic acid* and zinc chloride to 300° (B. **20**, R. 221) :



Aniline Pyro-mucic acid α-Naphthylamine.

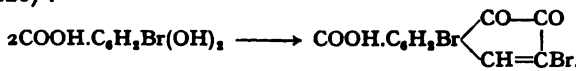
α-Naphthylamine is similarly formed on heating aniline hydrochloride with mannitol under pressure.

9. Two molecules of styrolene alcohol or phenyl-glycol can be condensed by dilute H_2SO_4 to β-phenyl-naphthalene (A. **240**, 137) :



Phenyl-acetaldehyde is an intermediate product.

10. The formation of a naphthalene derivative in the oxidation of bromo-proto-catechuic acid with nitric acid is peculiar. There is produced thereby a dibromo-β-naphtho-quinone-carboxylic acid (A. **293**, 120) :

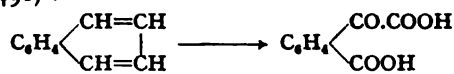


Decompositions of the Naphthalene Ring.

Naphthalene and most of its derivatives are converted by energetic oxidants into o-phthalic acid and substituted o-phthalic acids with destruction of one benzene nucleus. The oxidation is made easier by the introduction of an amido-group into the nucleus which is to be oxidised. Naphthols and their derivatives are decomposed by heating with alkalies, and oxidising metallic oxides to form phthalic and benzoic acids (C. 1903, I. 1106).

In many instances it has been possible, by moderating the oxidising action, to arrest the intermediate products of this reaction, or even the primary products in the breaking-down of the ring.

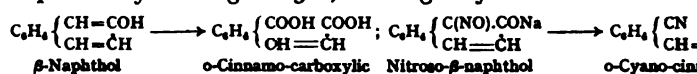
1. *Decomposition by Mild Oxidation.*—(*a*) Potassium permanganate oxidises naphthalene to phthalic acid and *phenyl-glyoxyl-o-carboxylic acid* (B. **28**, R. 490) :



Naphthalene Phenyl-glyoxyl-o-carboxylic acid.

(*b*) α- and β-Naphthols, oxidised with an alkaline permanganate solution, also yield o-carbo-phenyl-glyoxylic acid. β-Naphthol with most careful oxidation becomes *o-cinnamo-carboxylic acid*, along with other products (M. **10**. 115).

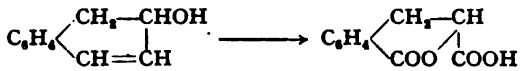
Besides these reactions we have the decomposition of sodium-nitroso-β-naphthol by heating to 250°, forming o-cyano-cinnamic acid :



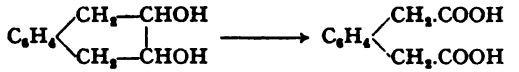
β-Naphthol o-Cinnamo-carboxylic acid. Nitroso-β-naphthol o-Cyano-cinnamic acid.

In the oxidation of α-nitro-naphthalene with potassium permanganate products appear which, in the process of reduction, yield, among other things, *isatin-carboxylic acid* $NH_2[3]C_6H_3\begin{cases}[1]COOH\\[2]COCOOH\end{cases}$ (B. **28**, 1641). Naphthalic acid becomes *phenyl-glyoxyl-dicarboxylic acid*.

(*c*) The decomposition of hydrogenised naphthalene derivatives occurs with special readiness; thus, permanganate changes dihydro-β-naphthol into *dihydro-iso-cumarin-carboxylic acid*, while potassium bichromate oxidises tetrahydro-naphthylene-glycol, in the cold, to *phenylene-o-diacetic acid* (B. **26**, 1833):

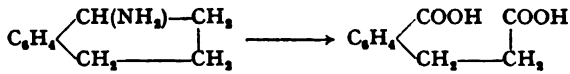


Dihydro-β-naphthol — Dihydro-iso-cumarin-carboxylic acid.

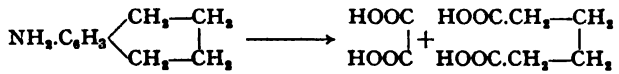


Tetrahydro-naphthylene-glycol — o-Phenylene-diacetic acid.

Potassium permanganate oxidises ac-tetrahydro-naphthylamine to *o-hydro-cinnamo-carboxylic acid*; ar-tetrahydro-naphthylamine, however, because of the oxidation of its amided benzene nucleus, is changed to *adipic acid* together with oxalic acid (B. **22**, 767):

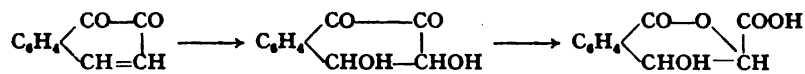


ac-Tetrahydro-naphthylamine — o-Carbohydro-cinnamic acid.



ar-Tetrahydro-naphthylamine — Oxalic acid — Adipic acid.

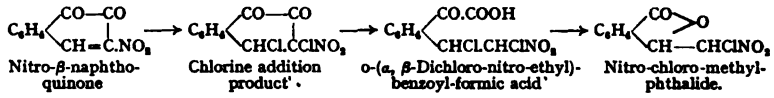
2. *Decomposition by Simultaneous Chlorination and Oxidation.*—The ring-decompositions, produced by the action of chlorine or hypochlorous acid upon β-naphtho-quinone and its derivatives, are very numerous. They proceed on lines analogous to the benzene-ring decompositions. Two groups may be distinguished in these changes: either the naphthalene ring first resolves itself into an indene ring, which subsequently by decomposition is converted into o-di-derivatives of benzene, as in the case of dichloro-naphtho-quinone (see below), or the break-down proceeds without the intermediate formation of indene, as in the case of β-naphtho-quinone or nitro-β-naphtho-quinone (see below) (Zincke, B. **27**, 2753, etc.). *Examples:* (*a*) β-Naphtho-quinone, by the action of hypochlorous acid, becomes dioxy-diketo-tetrahydro-naphthalene, which by the decomposition of the ring changes to the lactone of o-phenyl-glycerol-carboxylic acid (B. **25**, 3599):



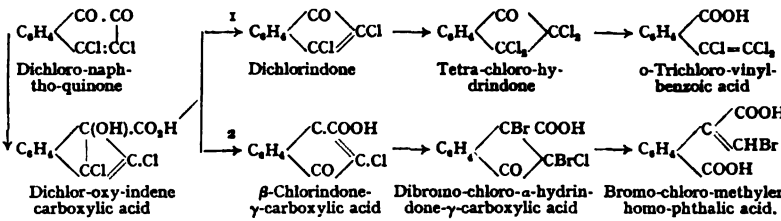
β-Naphtho-quinone — Dioxy-diketo-tetrahydro-naphthalene — o-Phenyl-glycerol-carboxylic acid lactone.

(*b*) With chlorine, nitro-β-naphtho-quinone first forms a chlorine addition product, which by ring-decomposition readily passes into

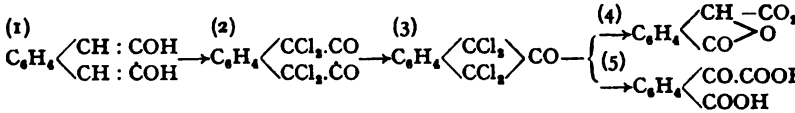
o-(α, β-dichloro-nitro-ethyl)-benzoyl-formic acid. Chromic acid oxidises the latter, with loss of hydrochloric acid and carbon dioxide, to nitro-chloro-methyl-phthalide, which can be directly formed by treating nitro-quinone with chlorine and water (B. **25**, R. 732) :



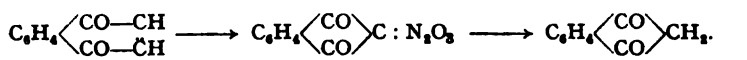
(*c*) Alkalies rearrange 3, 4-dichloro-β-naphtho-quinone to dichloroxy-indene-carboxylic acid. The latter can be decomposed (1) by changing it to dichlorindone with CrO_3, and tetrachloro-hydrindone, the chlorine addition product, when acted upon with alcoholic soda, becomes o-tri-chloro-vinyl-benzoic acid; or (2) if the acid be heated to 100°–110° with oil of vitriol it is converted into β-chlorindone-γ-carboxylic acid. The bromine addition product of the latter acid is decomposed by alkalies with the formation of α-chloro-bromo-methylene-homo-phthalic acid (B. **28**, R. 279) :



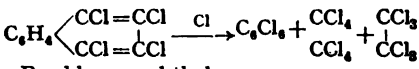
(*d*) 2, 3-Dioxy-naphthalin (1) yields under the action of chlorine tetrachloro-2, 3-diketo-tetrahydro-naphthalin (2), which is converted by bleaching-lime into tetrachloro-β-hydrindone (3); the latter is split up by alkalies to phthalide-carboxylic acid (4), and by concentrated HNO_3 to phthalonic acid (5) (A. **334**, 342) :



3. A transformation of the naphthalin nucleus into the indene nucleus has also been effected by the liquid nitrous acid upon α-naphtho-quinone; this first forms diketo-hydrindene-nitrosite, which, on careful treatment with water, passes into α, γ-diketo-hydrindene (B. **33**, 543) :

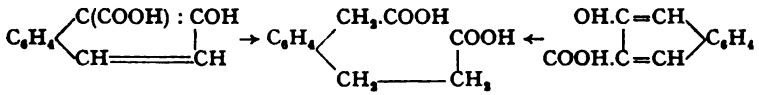


4. When perchloro-naphthalene is heated with $SbCl_5$ to 280°–300° it is resolved into perchloro-benzene, tetrachloro-methane, and hexa-chloro-ethane (B. **9**, 1486) :



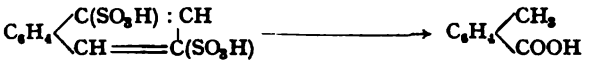
5. *Decomposition by Reduction in Alkaline Solution.*—A ring-decomposition analogous of that of salicylic acid (p. 49) is that under-

gone by 2, 1- and 2, 3-oxy-naphthoic acids (p. 679) when their alcoholic solutions are acted upon by metallic sodium (A. **286**, 268) :



2-Oxy-1-naphthoic acid — o-Phenylene-aceto-propionic acid — 2-Oxy-3-naphthoic acid.

6. Naphthalene-disulphonic acids, naphthylamine- and naphthol-sulphonic acids, containing the substituents in the 1, 3-position, sustain a remarkable decomposition into o-toluic acid when they are fused with caustic potash (B. **28**, R. 364) :



Naphthalene-1-3- disulphonic acid — o-Toluic acid.

m-Cresol (*Ch. Z.* 1895, No. 48) is similarly produced on fusing 1, 3, 6- and 1, 3, 8-naphthalene-trisulphonic acids with caustic potash.

Naphthalene $C_{10}H_8$, melting at 79° and boiling at 218°, occurs in coal-tar, and is obtained by crystallisation from that portion boiling from 180°–300°. It is purified by distillation with steam and sublimation. It dissolves with difficulty in cold alcohol, readily in hot alcohol and in ether. It crystallises and sublimes in shining plates. It is characterised by its great volatility and possesses a peculiar odour. It forms a crystalline compound $C_{10}H_8.C_6H_2(NO_2)_3.OH$ with *picric acid*, which melts at 149° (Fritzsche, J. **1857**, 456). m- and p-Dinitro-benzene, trinitro-benzene, trinitro-toluene, etc., form similar double compounds.

Naphthalene is applied technically in the preparation of phthalic acid and dye-substances. It is also used in carburetting water-gas. It is employed for itch, moths, etc., because of its strong antiseptic properties and its stupefying effect upon the lower animals.

As naphthalene has unsaturated linkages it will, under favourable conditions, take up hydrogen and chlorine ; the compounds thus produced will be discussed in conjunction with other hydro-naphthalene derivatives at the conclusion of the naphthalene group. Naphthalene, like benzene, is chlorinated, nitrated, and sulphonated by halogen, nitric acid, and sulphuric acid.

Naphthalene Homologues.—The methylated naphthalenes are present in coal-tar. Alkylic naphthalenes also result from the bromo-naphthalenes by the action of alkylogens and sodium, and from naphthalene by means of alkyl iodides or bromides and $AlCl_3$:

		M.p.	B.p.
α-Methyl-naphthalin .	$C_{10}H_7$-α-CH_3 . .	−20°	240°–243°
β-Methyl-naphthalin .	$C_{10}H_7$-β-CH_3 . .	+32°·5	241°–242° [1]
1, 4-**Dimethyl-naphthalin**	$C_{10}H_6$-1, 4-$(CH_3)_2$.	liquid	262°–264° [2]
α-Ethyl-naphthalin .	$C_{10}H_7$-α-C_2H_5 . .	,,	258°
β-Ethyl-naphthalin .	$C_{10}H_7$-β-C_2H_5 . .	−19°	251°
α-n-Propyl-naphthalin .	$C_{10}H_7$-α-$(CH_2)_2CH_3$.	liquid	274°
β-n-Propyl-naphthalin .	$C_{10}H_7$-β-$(CH_2)_2CH_3$.	,,	278°
α-n-Butyl-naphthalin .	$C_{10}H_7$-α-$(CH_2)_3CH_3$.	,,	282°
β-n-Butyl-naphthalin .	$C_{10}H_7$-β-$(CH_2)_3CH_3$.	,,	284°

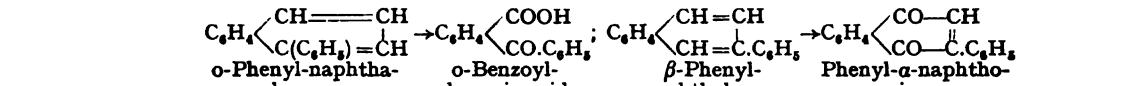
[1] B. **25**, R. 857. [2] B. **28**, R. 619.

		M.p.	B.p.
α-Iso-butyl-naphthalin	$C_{10}H_7$-α-$CH_2CH(CH_3)_2$.	liquid	137° (11 mm.)
β-Iso-butyl-naphthalin	$C_{10}H_7$-β-$CH_2CH(CH_3)_2$	,,	112° (6 mm.)
α-Phenyl-naphthalin .	$C_{10}H_7$-α-C_6H_5 . .	0°	325°
β-Phenyl-naphthalin .	$C_{10}H_7$-β-C_6H_5 . .	102°	347°.

α- and *β-Phenyl-naphthalenes* have been prepared by the action of diazo-benzene chloride upon naphthalene in the presence of Al_2Cl_6.

Similarly, *nitro-phenyl-naphthalene*, melting at 129°, is obtained from sodium nitro-phenyl-nitrosamine with naphthalene (B. **29,** 168).

β-Phenyl-naphthalene is also formed on conducting the vapours of bromo-benzene and naphthalene through tubes heated to redness ; also in the condensation of two molecules of phenyl-glycol (B. **26,** 1119, 1748), and in the distillation of β-phenyl-hydroxy-α-naphtho-quinone with zinc dust (A. **296,** 28). The constitution of the two isomeric phenyl-naphthalenes can be deduced from their oxidation products : α-phenyl-naphthalene yields o-benzoyl-benzoic acid, whereas β-phenyl-naphthalene yields phenyl-α-naphtho-quinone :



o-Phenyl-naphthalene → o-Benzoyl-benzoic acid ; β-Phenyl-naphthalene → Phenyl-α-naphtho-quinone.

Olefin - naphthalins.—**α-Vinyl - naphthalin** $C_{10}H_7.CH : CH_2$, b.p.$_{15}$ 137°, from α-naphthyl-magnesium bromide and acetaldehyde. **α-Alyl-naphthalin** $C_{10}H_7.CH_2.CH : CH_2$, b.p. 266°, from allyl bromide and α-naphthyl-magnesium bromide. On heating with alcoholic KOH it is transposed into the isomeric **α-propenyl-naphthalin** $C_{10}H_7.CH.CH : CH_3$, b.p.$_{10}$ 138°, which is also formed from α-naphthaldehyde, propionic anhydride, and Na propionate (C. 1897, II. 800 ; 1908, II. 1779). α- and **β-iso-propenyl-naphthalin** $C_{10}H_7.C(:CH_2)CH_3$, α- b.p.$_8$ 125°, β- m.p. 45°–47°, b.p.$_7$ 139°, are formed from α- and β-naphthyl-methyl-ketone with CH_3MgI ; the β-compound direct, and the α-compound by way of α-naphthyl-dimethyl-carbinol with acetic anhydride (C. 1901, I. 1321).

Substituted Naphthalenes.

1. *Halogen Derivatives.*—These are formed (1) by the direct substitution of the hydrogen atoms by halogens ; (2) by the replacement of NH_2 groups in amido-naphthalenes by halogens, following Griess' reaction (p. 60) ; (3) by the replacement of OH as well as of SO_3H and NO_2 groups in oxy-, nitro-, or sulpho-derivatives of naphthalene on heating them with PCl_5. The latter reaction is useful for determining positions in naphthalene- and naphthol-sulphuric acids.

The union of the halogen atoms, and also that of the other substituents, like NO_2, SO_3H (cp. B. **26,** 3028), in naphthalene derivatives are, as a rule, less stable than in the corresponding benzene derivatives.

Fluoro-naphthalenes $C_{10}H_7F$: the α-form boils at 216°, the β- melts at 59° and boils at 213°.

Chloro-naphthalenes $C_{10}H_7Cl$: the α- boils at 263°, while the β- melts at 56° and boils at 265°. α-Chloro-naphthalene is produced (1) in chlorinating boiling naphthalene ; further, (2) by action of alcoholic potash upon naphthalene dichloride ; (3) from naphthalene-α-sulphonic acid and PCl_5 ; (4) from α-amido-naphthalene. β-Chloro-naphthalene

is prepared from β-amido-naphthalene or from β-naphthol. **Dichloro-naphthalenes** $C_{10}H_6Cl_2$: The ten possible isomerides are known : 1, 2- melts at 35° and boils at 281° ; 1, 3- melts at 61° and boils at 289° ; 1, 4- melts at 68° and boils at 287° ; 1, 5- melts at 107° ; 1, 6- melts at 48° ; 1, 7- melts at 62° and boils at 286° ; 1, 8- melts at 83° ; 2, 3- melts at 120° ; 2, 6- melts at 135° and boils at 285° ; 2, 7- melts at 114° (B. **24,** 3475, R. 653, 704, 709 ; **26,** R. 536).

Trichloro-naphthalenes.—There are fourteen isomerides ; see B. **29,** R. 227.

Pentachloro-naphthalene $C_{10}H_3Cl_5$ melts at 168°. **Perchloro-naphthalene** $C_{10}Cl_8$ melts at 203° and boils at 403°.

Bromo-naphthalenes $C_{10}H_7Br$: the α-variety melts at 5° and boils at 279°, while the β-variety melts at 59° and boils at 282°. **Iodo-naphthalenes** $C_{10}H_7I$: the α-body is an oil, boiling at 305° ; the β-body melts at 54·5°. α-Iodo-naphthalene is obtained by the introduction of iodine into a carbon bisulphide solution of mercury dinaphthyl $Hg(C_{10}H_7)_2$. See B. **29,** 1408, for the bromo-iodo-naphthalenes, and B. **27,** 599, for the **naphthyl-iodo-chlorides** and **iodoso-naphthalenes.** Consult B. **29,** 1573, for **β-iodo-naphthalene.** Iodo-naphthalene and naphthyl-phenyl-iodonium hydroxide, see B. **29,** 1573 ; **33,** 692 ; C. 1901, II. 750.

2. *Nitro-naphthalenes.*—**α-Nitro-naphthalene** $C_{10}H_7$-α-NO_2 consists of yellow needles, melting at 61° and boiling at 304°. It is produced on treating naphthalene with nitric acid at the ordinary temperature. When heated with PCl_5 it yields α-chloro-naphthalene. Chromic acid oxidises it to v-nitro-phthalic acid. **β-Nitro-naphthalene,** melting at 79°, is derived from β-nitro-naphthylamine by replacing the NH_2 group by hydrogen, or, better, from β-diazo-naphthalene nitrite $C_{10}H_7N$ =N.O.NO, by means of Cu_2O (B. **20,** 1494 ; **36,** 4157). Transformation into 4, 1- and 2, 1-nitroso-naphthol, see A. **355,** 299. Different **dinitro-naphthalenes** are obtained by the nitration of naphthalene at high temperatures. Consult B. **29,** 1243, 1521, for the separation of the 1, 5- and 1, 8-compounds. The 1,5-(α-) compound melts at 216° ; the 1, 8-(β-) body melts at 170°, and when heated with potassium cyanide yields potassium *naptho-cyaminate* $C_{28}H_{17}N_8O_9K$. The two dinitro-naphthalenes, when heated with sulphuric acid and reducing agents, form *naphthazarin* or dioxy-naphtho-quinone (B. **27,** R. 959). **1, 8-(γ-) Dinitro-naphthalene,** melting at 144°, is obtained from amido-dinitro-naphthalene. At very low temperatures (−50° to −55°) nitric acid and naphthalene form various dinitro-naphthalenes (B. **26,** R. 362). When naphthalene or dinitro-naphthalenes are boiled for some time with fuming nitric and sulphuric acids (B. **28,** 367) **tri-** and **tetranitro-naphthalenes** are produced. These explode partly with violence on heating.

3. *Nitroso-naphthalenes.* — **Mononitroso-naphthalene** $C_{10}H_7.NO$, melting at 89° and decomposing at 134°, results from the action of nitrosyl bromide upon mercury dinaphthyl, or by oxidation of naphthyl-hydroxylamine with Ag_2O or PbO_2 (B. **41,** 1937).

1, 4-Dinitroso-naphthalene is a powder exploding at 120°, and is produced when α-naphtho-quinone-dioxime is oxidised with red prussiate of potash. **1, 2-Dinitroso-naphthalene,** melting at 127° (B. **19,** 349 ; **21,** 434), is similarly formed from β-naphtho-quinone-dioxime.

4. *Amido-naphthalenes, Naphthylamines.*—(*a*) *Primary Amines.*—The naphthylamines, in contrast to the anilines, are very easily obtained by heating the oxy-naphthalenes or naphthols with ammonia-zinc chloride.

They are also formed by fusing naphthalene-sulphonic acids with sodium amide. Naphthalene itself in the presence of phenol at 220° yields α-naphthylamine and 1, 5-naphthylene-diamine (B. **89**, 3011).

The acid sulphurous acid esters of naphtholene and naphthol derivatives are transformed by treatment with ammonia in aqueous solution into naphthylamines at temperatures as low as 100°. This action is reversed by boiling with alkaline bisulphite (*J. pr. Ch.* 2, **69**, 49):

$$C_{10}H_7.OSO_2Me \underset{\leftarrow SO_2HMe}{\overset{NH_3}{\longrightarrow}} C_{10}H_7.NH_2.$$

α-Naphthylamine $C_{10}H_7$-α-NH_2, melting at 50° and boiling at 300°, results from the reduction of α-nitro-naphthalene, or on heating α-naphthol with $ZnCl_2$ or $CaCl_2$-ammonia to 250°, and is synthetically produced when aniline and zinc chloride are heated with pyro-mucic acid. It crystallises in flat needles, which are especially beautiful when they separate from aniline. It acquires a red colour on exposure to the air, sublimes readily, and possesses a pungent odour. In general, it behaves exactly like the phenylamines.

Sodium in amyl alcohol reduces it to α-tetrahydro-naphthylamine. It is oxidised to α-naphtho-quinone when boiled with chromic acid. Oxidising agents (chromic acid, ferric chloride, silver nitrate) produce an azure-blue precipitate in the solutions of its salts: *oxy-naphthylamine* $C_{10}H_9NO$ (A. **129**, 255).

In α-naphthylamine derivatives the amido-group can be replaced by the hydroxyl group by treating with H_2SO_3 and alkali (C. 1900, II. 359).

β-Naphthylamine, melting at 112° and boiling at 294°, results from β-naphthol and $ZnCl_2$-ammonia. It is odourless, and is not coloured by ferric chloride and the like. Potassium permanganate oxidises it to phthalic acid. β-Tetrahydro-naphthylamine is formed by its reduction.

Secondary and Tertiary Naphthylamines.—Naphthyl-alkylamines are formed, analogous to the alkyl-anilines, from the naphthylamines with alkylogens, or upon heating the naphthylamine hydrochlorides with alcohols. Also from the sulphurous esters of naphthols by heating with aliphatic amines. The β-naphthol, but not the α-naphthol esters, react in this way with aromatic amines (*J. pr. Ch.* 2, **70**, 345; **71**, 433).

α-Naphthyl-methylamine $C_{10}H_7NH.CH_3$, boils at 293°; **α-naphthyl-ethylamine** boils at 303°; **β-naphthyl-dimethylamine** $C_{10}H_7$-β-$N(CH_3)_2$ melts at 46° and boils at 305° (B. **18**, 2053). The **phenyl-naphthylamines** $C_{10}H_7.NH.C_6H_5$ are formed when the hydrochlorides of α- and β-naphthylamines are heated with aniline and zinc chloride. On heating the naphthylamines with zinc chloride or with HCl to 180°–190°, or with α- and β-naphthol, various *dinaphthylamines* result. **β, β-Dinaphthylamine** $C_{10}H_7$-β-NH-β-$C_{10}H_7$, melting at 171° and boiling at 471°, occurs as a by-product in the technical manufacture of β-naphthylamine. Heated to 150° with concentrated hydrochloric acid, it breaks down into β-naphthylamine and β-naphthol. Heated with sulphur it forms thio-dinaphthylamine $NH(C_{10}H_6)_2S$, corresponding to

thio-diphenylamine. When sulphuric acid (80 per cent.) acts upon β-naphthylamine in the presence of oxidising agents, two naphthalene nuclei unite and *naphthidine* $(C_{10}H_6.NH_2)_2$ results (B. **25,** R. 949).

The *acid derivatives of the naphthylamines* show great similarity to those of the anilines. The **naphthyl-benzene sulphamides** $C_{10}H_7.NH.SO_2.C_6H_5$ manifest a rather remarkable deportment, similar to that of the naphthols, in that they dissolve in the alkalies, and unite similarly with diazo-salts, etc. (B. **27,** 2370). Consult B. **25,** R. 9, upon **naphthyl-carbamine-chlorethyl esters** $C_{10}H_7.NH.COOC_2.H_4Cl$ and their transposition products. See B. **29,** R. 184, for the α-naphthylamine derivatives of succinic, tartaric, and citric acids.

Substituted Naphthylamines.—Haloid naphthylamines result by direct substitution, or by the action of ammonia upon substituted naphthols. **1, 2-** and **1, 4-nitro-naphthylamines** are formed by the nitration of aceto-α-naphthylamine and its subsequent saponification. The 1, 4-*body* melts at 191°. It is oxidised to α-naphtho-quinone. It forms α-nitro-naphthalene by the elimination of the NH_2 group. Boiling potassium hydroxide converts α-nitro-naphthalene into 1, 4-nitro-naphthol (B. **19,** 796 ; **25,** R. 432). The 1, 2-*compound* melts at 144°, and yields β-nitro-naphthalene and 2, 1-nitro-naphthol.

1-Nitro-2-naphthylamine, melting at 127°, is formed by the nitration of aceto-β-naphthylamine and subsequent saponification of the aceto-derivative. Nitrous acid and alcohol convert it into α-nitro-naphthalene. **2, 5-** and **2, 8-Nitro-naphthylamines** (B. **25,** 2076) are produced when β-naphthylamine nitrate is introduced into concentrated sulphuric acid.

Naphthylene Diamines.—*Diamido-naphthalenes, naphthylene-diamines,* are obtained by the reduction of dinitro- and nitro-amido-naphthalenes, also by the decomposition of amido-azo-naphthalenes, and when dioxy-naphthalenes and amido-oxy-naphthalenes are heated with ammonia (B. **21,** R. 839 ; **22,** R. 42 ; **26,** 188).

The o-naphthylene-diamines adapt themselves like the o-phenylene-diamines to condensation reactions, in that they form *naphtho-derivatives of heterocyclic rings.* To a certain degree the o-naphthylene-diamines in this respect resemble the 1, 8- or *peri*-compounds (p. 651).

1, 2-Naphthylene-diamine, melting at 98°, is obtained by reduction from β-nitro-α-naphthylamine and β-naphtho-quinone-dioxime. **2, 3-Naphthylene-diamine,** melting at 191°, is derived from 2, 3-dioxy-naphthalene by the action of ammonia at 240°. These two bodies yield **naphtho-azimides** with nitrous acid, *anhydro*-bases with carboxylic acids, *quinoxalins* with o-diketones, etc. (B. **25,** 2714 ; **26,** 188 ; **27,** 761). Perfectly similar hetero-ring-formations are exhibited by **1, 8- (peri-) naphthylene-diamine,** melting at 67° and obtained from 1, 8-dinitro- or 1, 8-dioxy-naphthalene ; however, it does not, in contrast to the o-diamines, condense with o-diketones, like phenanthra-quinones, forming **azines** (B. **22,** 861).

1, 8-Naphthylene-diamine melts at 96° ; has been obtained by nuclear synthesis by the action of concentrated H_2SO_4 upon γ-phenyl-β-imino-butyro-nitrile (B. **28,** 1953). 1, 3-(*m*)-*Naphthylene-diamine derivatives* are derived from naphthylamine-sulphonic acids, which contain the SO_3H group in the meta-position with reference to NH_2, by the action of amines.

(1, 4)-Naphthylene-diamine, melting at 120°, results from the reduction of α-nitro-naphthylamine, and the decomposition of α-amido-azo-naphthalene, by tin and hydrochloric acid. Ferric chloride converts it into α-naphtho-quinone, and bleaching-lime changes it to naphtho-quinone dichlorimine.

1, 5-Naphthylene-diamine, m.p. 189°, has also been obtained from α-naphthylamine, and 1, 6-*naphthylene-diamine*, m.p. 78°, from β-naphthylamine by fusing with $NaNH_2$ (B. **39,** 3021).

1, 7-Naphthylene-diamine, m.p. 117°; see B. **25,** 2082. **2, 6-Naphthylene-diamine,** m.p. 216°; see A. **323,** 130. **2, 7-Naphthylene-diamine,** m.p. 159° (*J. pr. Ch.* 2, **69,** 89).

5. *Diazo- and Azo-compounds of Naphthalene.*—By the action of HNO_2 and $NaNO_2$ upon the salts of naphthylamines, diazo-compounds are obtained which, like the benzene-diazo-compounds, form azo-dyes with anilines and phenols. The diazo-amido-compounds probably formed cannot be isolated. But α- and β-naphthalene-diazonium chloride and aniline give α- and **β-naphthalin-diazo-amido-benzol,** naphthyl-phenyl-triazene $C_{10}H_7N : N.NHC_6H_5$, m.p. 84° and 150° with decomposition. The α-body has also been obtained by other methods (B. **40,** 2400).

β-Diazo-naphthalin-imide, m.p. 33°; see C. 1908, I. 527 (*J. pr. Ch.* 2, **76,** 461). **1-Nitro-2-diazo-naphthalin-imide** $C_{10}H_6[1]NO_2[2]N_3$, m.p. 117°, decomposes on heating with alcohol or glacial acetic acid into N_2 and 1, 2-dinitroso-naphthalene (C. 1908, I. 526).

β-Diazo-naphthalene acid, *β-naphthyl-nitramine* $C_{10}H_7$-β-$NH.NO_2$, yields on transposition 2-amido-1-nitro-naphthalene (B. **30,** 1262).

Azo-naphthalenes.—The reduction of nitro-naphthalenes to azoxy- and azo-naphthalenes is less straightforward than in the case of the nitro-benzols. α-Nitro-naphthalene gives on reduction with zinc dust in neutral solution naphthyl-hydroxylamine and **αα-azoxy-naphthalene** $C_{10}H_7[\alpha]N_2O[\alpha]C_{10}H_7$, m.p. 127°. The latter on further reduction yields **αα-azo-naphthalene,** m.p. 190°, red needles (A. **321,** 61).

ββ-Azo-naphthalene, m.p. 208°, red flakes, is formed besides **dinaphtho-ortho-diazin** $\begin{matrix} C_{10}H_6\text{—}N \\ | \quad\quad \| \\ C_{10}H_6\text{—}N \end{matrix}$ and 2, 2-diamido-1, 1-dinaphthyl by reduction of β-nitro-naphthalene (B. **36,** 4153).

Benzol-azo-naphthalene $C_{10}H_7.N_2C_6H_5$, m.p. 65°.

o-Toluene-azo-naphthalene $C_{10}H_7.N_2.C_7H_7$ melts at 52° (B. **26,** 143).

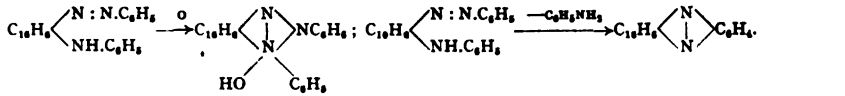
Naphthyl-azo-acetic ester $C_{10}H_7.N_2.CH(COCH_3)CO_2R$, melting at 94°, is formed from diazo-naphthalene chloride and sodium aceto-acetic ester. Caustic potash changes it to naphthyl-acetone, and by the acid decomposition it is resolved into *naphthyl-azo-acetic acid* (B. **24,** R. 571).

Amido-azo-naphthalenes—**α-Amido-azo-naphthalene** $C_{10}H_7$-α-N_2-α-$C_{10}H_6$-α_1-NH_2, melting at 175°, is formed by adding sodium nitrite (1 mol.) to the aqueous solution of naphthylamine hydrochloride (2 mol.); the diazo-amido-naphthalene $C_{10}H_7.N_2.NH.C_{10}H_7$ first formed undergoes a molecular rearrangement. Tin and hydrochloric acid resolve α-amido-azo-naphthalene into α-naphthylamine and (1, 4)-naphthylene-diamine. *Naphthalene red* belongs to the safranine dyes and is produced when α-amido-azo-naphthalene is heated with Na-naphthylamine hydrochloride.

β-Amido-azo-naphthalene, from β-naphthylamine, melts at 156° (B. **19,** 1282).

α-Naphthylamine-azo-benzene-sulphonic acid $C_6H_4(SO_3H).N_2.C_{10}H_6.NH_2$, from sulphanilic acid and naphthylamine hydrochloride, is coloured orange by caustic potash and *red* by acids (test for nitrous acid).

The o-azo-compounds of β-naphthyl-alphylamines, like **benzene-azo-β-naphthyl-phenylamine** $C_{10}H_6\begin{cases}[1]N:N.C_6H_5\\[2]N:N.C_6H_5\end{cases}$, when oxidised form *ammonium bases* of the *pseudo-azimide group*, and when heated they split off aniline, forming *naphtho-phenazines* (A. **28,** 328) :



Compare further B. **18,** 3132 ; **20,** 1167 ; **24,** R. 765, for the constitution of the products resulting from the action of diazo-salts upon β-napthylamines, which are sometimes viewed as β-quinone derivatives.

6. *Hydrazin Derivatives of Naphthalene.*—**Hydrazo-naphthalene** $C_{10}H_7.NH.NH.C_{10}H_7$, melting at 275°, corresponds to hydrazo-benzene. It is formed on boiling azo-naphthalene with alcoholic sodium hydroxide and zinc dust. When digested with hydrochloric acid it changes to the isomeric **naphthidin** or diamido-dinaphthyl and 1, 1-diamido-2, 2-dinaphthyl or dinaphthylin (B. **88,** 136) ; **ββ-hydrazo-naphthalin**, m.p. 141°, is transposed into 2, 2-*diamido*-1, 1-*dinaphthyl* by both acids and alkalies (cp. benzidin transposition).

Naphthyl-hydrazins $C_{10}H_7.NH.NH_2$ are derived from the diazo-chlorides of the two naphthylamines by the action of stannous chloride and hydrochloric acid (B. **19,** R. 303). The α-compound melts at 117°, the β-modification at 125°. They unite with the aldehydes and ketones forming hydrazones ; these form naphthindol compounds by condensation, and manifest throughout the tendency to form derivatives and hetero-ring formations similar to those shown by the phenyl-hydrazins (B. **19,** R. 831 ; **22,** R. 672). On β-naphthyl-hydrazones of sugars, see B. **35,** 1841. **2, 3-Naphthylene-dihydrazin** $C_{10}H_6[2, 3](NHNH_2)_2$, m.p. 156°, see B. **88,** 266 ; *J. pr. Ch.* 2, **76,** 205.

7. *Sulphonic Acids.*—On digesting naphthalene with sulphuric acid we have formed α- and **β-naphthalene-sulphonic acids.** At lower temperatures (80°) the α-acid, melting at 90°, predominates, while at about 160° and with an excess of sulphuric acid the β-acid, melting at 161°, is the chief product. When heated with sulphuric acid the α-acid passes into the β-variety. They may be separated by means of the calcium or lead salts. The free acids are crystalline, and deliquesce readily. The α-acid decomposes upon heating with dilute hydrochloric acid to 200° into naphthalene and sulphuric acid, whereas the β-acid remains unaltered.

The *α-sulpho-chloride* melts at 66° and boils at 185° (13 mm.). The *β-sulpho-chloride* melts at 76° and boils at 201° (13 mm.) (*J. pr. Ch.* 2, **47,** 49). Protracted heating of naphthalene with concentrated sulphuric acid produces two isomeric disulpho-acids : 2, 6- and 2, 7-.

Naphthalene-disulphonic Acids.—They are separated by crystallising their chlorides from benzene (B. **9,** 592). Additional disulphonic acids of naphthalene have been prepared by sulphonating the naphthalene-

monosulphonic acids, by oxidising thio-naphthol-sulphonic acids, from the naphthylamine-disulphonic acids, etc. A series of **naphthalene-trisulphonic acids** has been made by similar indirect methods (B. **24,** R. 654, 707, 715; **27,** R. 81; **32,** 3186; *Proc.* **126,** 168). **Chloro-naphthalene-sulphonic acids** have been obtained in part by sulphonating the chloro-naphthalenes, and in part by replacing the NH_2 group of the naphthyl-amine-sulphonic acids by halogens (B. **24,** R. 658, 707; **25,** 2479; *Ch. Z.* 1895, 1114). **Nitro-naphthalene-sulphonic acids** are obtained by sulphonating the nitro-naphthalenes or nitrating the chlorides of the sulphonic acids (B. **26,** R. 536).

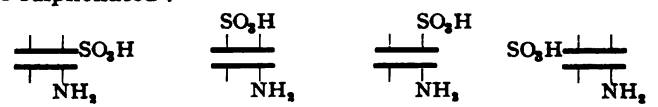
Some *naphthylamine-sulphonic acids* possess technical value, inasmuch as they form desirable and valuable dyes by combining with the tetrazo-compounds of the benzidine series :

(*a*) α-Naphthylamine, treated at 130° with an excess of concentrated sulphuric acid, forms **1, 4-naphthylamine-sulphonic acid, naphthionic acid,** which can also be prepared from nitro-naphthalene with ammonium sulphite by simultaneous reduction and sulphonation (*Ch. Z.* 1895, 1114; A. **78,** 31). The acid crystallises with $\frac{1}{2}H_2O$ and dissolves sparingly in water. Its *sodium salt* has the formula $C_{10}H_6(NH_2)SO_3Na + 4H_2O$. When the acid combines with the tetrazo-derivative of benzidine *Congo red* is produced. Tin and hydrochloric acid decompose the latter with the formation of 1, *2-naphthylene-diamine-4-sulphonic acid.* See B. **29,** 1978, for additional naphthylene-diamine-sulphonic acids.

If α-naphthylamine be digested with sulphuric acid at 130° for some time there results, instead of the 1, 4-acid, **1, 5-napthylamine-sulphonic acid,** *naphthal-idinic acid,* and this finally gives place to the 1, 6-acid (B. **26,** R. 534). **1, 8-** or **Peri-naphthylamine-sulphonic acid** is obtained from peri-nitro-sulphonic acid. The derivatives of the 1, 8-acid show a tendency to part with water with the production of *sultams—e.g.* $(SO_3H_2)C_{10}H_4\langle{}^{SO_2}_{NH}$, **1, 8-naphth-sultam, 2, 4-disulphonic acid** $(SO_3H)_2C_{10}H_2\langle{}^{SO_2}_{NH_2}$, **1, 8-naphth-sultam-trisulphonic acid** (B. **27,** 2137). Peri-amido-naphthol derivatives are produced when these sultams are fused with caustic potash (B. **28,** R. 636).

Dimethyl-α-naphthylamine-sulphonic acids $(CH_3)_2NC_{10}H_6SO_3H$, see B. **35,** 976. Naphthionates condense easily with aldehydes to RCH : $NC_{10}H_6SO_3Me$ (C. 1901, II. 903).

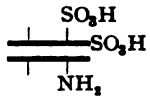
(*b*) Four different, isomeric, *β-naphthylamine-sulphonic acids* (A. **275,** 262) are produced, according to the temperature, when β-naphthyl-amine is sulphonated :



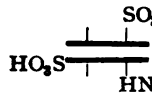
α-acid (Baden acid) — β-acid (Brönner's acid) — F- or δ-acid — γ-acid (Dahl's acid).

These acids can also be prepared by the action of ammonia upon the corresponding naphthol-sulphonic acids (p. 669). The β- and the F- or δ-acids are particularly valuable, because by their combination with

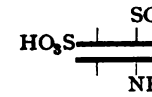
o-tetrazo-ditolyl beautiful red dyes having a blue tinge result. Certain *β-naphthylamine-disulphonic acids* are technically important :



Amido-sulphonic acid G (B. **24**, R. 716)



Amido-sulphonic acid R (B. **24**, R. 707)



δ-Amido-sulphonic acid (B. **24**, R. 715).

See B. **27**, 1193, for additional β-naphthyl-amido-poly-sulphonic acids. These β-naphthylamine-sulphonic acids, which contain a sulpho-group in the m-position with reference to the NH_2 group, readily exchange the sulpho-group for the amine residue when they are heated with amines (B. **28**, R. 311).

1, 4-Diazo-naphthalene-sulphonic acid $C_{10}H_6\langle^{SO_2}_{N_2}\rangle O$, *diazo-naphthionic acid*, is produced by the action of nitrous acid upon naphthionic acid. It forms *rocellin* by combining with α-naphthol, and *azorubin* S by its union with α-naphthol-α-sulphonic acid.

By the union of various azo-naphthalene-diazo-sulphonic acids—*e.g.* $C_{10}H_7N_2.C_{10}H_5\langle^{N_2}_{SO_2}\rangle O$—with naphthol-monosulphonic acid, azo-black dyes—*e.g.* ***naphthol-black***, ***wool-black***, etc.—result.

8. *Naphthalene-sulphinic acids* are derived by the reduction of the chlorides of sulpho-acids ; on treating naphthalene-diazonium salts with SO_2 and powdered Cu ; or by the action of SO_2 upon naphthalene in the presence of $AlCl_3$ (B. **32**, 1141 ; **41**, 3319). **α-Naphthalene-sulphinic acid** $C_{10}H_7.SO_2H$ melts at 84°, while the β-acid melts at 105° (B. **26**, R. 271). These acids behave just like the benzene-sulphinic acids (B. **25**, 230). Mixed ***naphthyl-sulphones*** are prepared from their salts by the action of alkyl bromides (B. **29**, R. 979).

9. *Naphthols.*—The oxy-derivatives of naphthalene or naphthols in general show a deportment similar to that of the phenols. However, their hydroxyl group is more reactive. They readily yield naphthyl-amines with ammonia. They form esters and ethers more easily than the phenols (B. **15**, 1427 ; C. 1900, I. 131, 349). The naphthols occur in coal-tar (A. **227**, 143).

α-Naphthol $C_{10}H_7$-α-OH melts at 95°, boils at 278°–280°, and results from α-naphthalene-sulphonic acid by fusing with potash, and from α-naphthylamine by means of the diazo-compound, and upon fusing α-naphthalene-sulphonic acid with alkalies. Its formation from phenyl-iso-crotonic acid is very noteworthy. It is soluble with difficulty in hot water, readily in alcohol and ether, crystallises in shining needles, has the odour of phenol, and is readily volatilised. Ferric chloride precipitates violet flakes of dinaphthol $C_{20}H_{12}(OH_2)$ from its aqueous solution. Nitrous acid converts it into 2, 1- and 4, 1-nitroso-naphthol ; chlorine in acetic acid changes it to various chlorinated naphthols and keto-hydro-naphthalenes ; potassium chlorate and hydrochloric acid oxidise it to dichloro-naphtho-quinone (A. **152**, 301) ; metallic sodium and alcohol reduce it to ar-tetrahydro-naphthol (p. 412), while potassium permanganate in alkaline solution breaks it down into carbo-phenyl-glyoxylic acid. The *acetate* $C_{10}H_7$-α-$O.C_2H_3O$ melts at 46°. See B. **28**, 3049, for the carbonate and phosphate.

β-Naphthol $C_{10}H_7$-β-OH, melting at 122° and boiling at 286°, is derived from β-naphthalene-sulphonic acid, or β-naphthylamine. It is readily soluble in hot water and crystallises in leaflets. Ferric chloride imparts a greenish colour to the solution and separates a dinaphthol. Nitrous acid and β-naphthol yield 1, 2-*nitroso-naphthol*. The *acetate* $C_{10}H_7$-β-OC_2H_3O melts at 70°. On mixing glacial acetic solution of β-naphthol and mercury acetate we obtain β-oxy-naphthyl-mercuric acetate $C_{10}H_6(OH).Hg.OCOCH_3$ (B. **31,** 2624).

The *bismuth salt* of β-naphthol has been recommended, under the name of *orpholum*, as an intestinal antiseptic.

Naphthol-alkyl ethers are formed when the naphthols are heated with alcohols and hydrochloric acid to 150° (B. **15,** 1427), or from naphthol-alkali salts with halogen alkyls or alkyl sulphates (B. **34,** 3172)

α-Naphthol-ethyl ether boils at 277°. **β-Naphthol-methyl ether** and **ethyl ether** have been called *Jara-Jara* and *neroline* and been used in perfumery (B. **26,** 2706). α- and **β-Dinaphthyl ethers** melt at 110° and 106° (B. **13,** 1840; **14,** 195; C. 1906, I. 364). α- and **β-Naphthyl-phenyl ether,** m.p. 55° and 93°, from the diazo-naphthalenes with phenol (C. 1902, II. 1470). α- and **β-Naphthoxy-acetic acid** $C_{10}H_7OCH_2COOH$, cp. B. **34,** 3191.

Naphthol homologues, such as **2, 1- and 3, 1-methyl-naphthol** $C_{10}H_6(CH_3)OH$, melting at 80° and 92°, have been prepared from phenyl-α- and -β-methyl-iso-crotonic acids (A. **255,** 272). **1, 4-Dimethyl-3-naphthol** $C_{10}H_5(CH_3)_2OH$, melting at 136°, is obtained from *santonin* (p. 724) (B. **28,** R. 116, 619; **31,** 1675). **1, 2-Methyl-naphthol** $C_{10}H_6[1]CH_3[2]OH$, m.p. 110°, from β-dinaphthol-methane by reduction with zinc dust and soda. HNO_2 has a peculiar action upon 1, 2-methyl-naphthol and its substitution products, producing either o-quinitrols or o-methylene-quinones. **1, 2-Methyl-naphtho-quinitrol** $C_{10}H_6[2]:O[1](NO_2)CH_3$, m.p. 60°, heated above its m.p., gives **1, 2-methyl-naphtho-quinol**, m.p. 89°, also obtained direct from 1, 2-methyl-naphthol by oxidation with CrO_3 in glacial acetic acid (C. 1907, II. 1415). **1, 2-Naphtho-methylene-quinone** $C_{10}H_6[2]:O[1]:CH_2$, m.p. 132°, yellow needles, shows a reaction inertia resembling that of the o-methylene-quinones of the benzene series (B. **39,** 435; **41,** 2614).

Substituted Naphthols.—Substituted α-naphthols can be synthesised from the substituted phenyl-iso-crotonic acids (cp. B. **26,** R. 537). Otherwise they are made by methods similar to those adopted with the substituted phenols (p. 193).

Nitro-naphthols.—**4, 1-Nitro-naphthol** $C_{10}H_6[4](NO_2)[1]OH$, melting at 164°, and **2, 1-nitro-naphthol** $C_{10}H_6[2]NO_2[1]OH$, melting at 195°, result from the oxidation of 4, 1- and 2, 1-nitroso-naphthol with potassium ferricyanide or nitric acid (B. **25,** 973), or by boiling the corresponding nitro-naphthylamines with caustic potash.

2, 4-Dinitro-α-naphthol, melting at 138°, is produced by the action of nitric acid upon these nitro-naphthols or upon naphthalene-α-sulphonic acid, α-naphthylamine, and α-naphthol-disulphonic acid (A. **152,** 299). It is almost insoluble in water, sparingly soluble in alcohol and in ether, decomposes alkaline carbonates, and forms yellow salts with one equivalent of base. The salts dye silk a beautiful golden yellow. The *sodium salt* $C_{10}H_5(NO_2)_2.ONa+H_2O$ finds use in dyeing,

under the name of *naphthalene yellow* (Martius yellow), and is frequently used to colour foods. The *potassium salt* of dinitro-naphthol-sulphonic acid, $C_{10}H_4(NO_2)_2\begin{cases}[1]OK\\[8]SO_3K\end{cases}$ (B. **24,** R. 709), obtained by the nitration of naphthol-trisulphonic acid, is *naphthol yellow.*

Trinitro-α-naphthol melts at 177°.

α-Nitro-β-naphthol, melting at 103°, is produced in the oxidation of α-nitroso-β-naphthol, or from nitro-β-naphthylamine by the action of caustic potash. See B. **25,** 2079, R. 670, and **31,** 2418, for other nitro-β-naphthols and -naphthol ethers.

Amido-naphthols.—These are derived by the reduction of nitro-naphthols, by the action of ammonia upon dioxy-naphthalenes, the decomposition of naphthol-azo-compounds, etc., etc., from dioxy-naphthalenes with NH_3, from naphthylamino-sulphonic acids by fusion with potash, from naphthol-sulphonic acids, and direct from naphthalene by fusion with Na amide (B. **39,** 3006).

In the isonuclear, particularly the 1, 3-amido-naphthols, the NH_2 group is more readily displaced than in the heteronuclear isomerides.

(1, 4)-Amido-α-naphthol $C_{10}H_6(NH_2).OH$ results from the reduction of (1, 4)-nitro-naphthol, and by the decomposition of α-naphthol orange $C_{10}H_6(OH).N_2.C_6H_4.SO_3H$. It is very unstable. It yields α-naphtho-quinone by oxidation.

Its *ethyl ether* $C_{10}H_6(OC_2H_5)NH_2$ melts at 96°. 4-*Acetamido*-1-*naphthol, naphthacetol,* melting at 187°, is especially well adapted for the production of pure naphthol-azo-dyes. 4-*Acetamino*-1-*naphthol-ethyl ether, naphthacetin,* melts at 189° (B. **25,** 3059).

2-Amido-α-naphthol, from 2, 1-nitro-naphthol, oxidises in the air to imido-oxy-naphthylamine or β-naphtho-quinonimide $C_{10}H_6\langle{}^{O}_{NH}$, $C_{10}H_6\langle{}^{NH}_{O}$, forming violet leaflets.

2, 1-Amido-naphthol yields *anhydro-bases* or *naphthoxazoles* (see B. **25,** 3430) with carboxylic acids, etc.

2-Diazo-α-naphthol, β-naphtho-quinone-diazide $C_{10}H_6\begin{cases}[2]\langle{}^{N}_{N}\\[1]:O\end{cases}$, yellow needles, m.p. 77°, from 1-chloro-2-naphthalene-diazonium sulphate on standing in aqueous solution; cp. quinone diazide (C. 1903, I. 401).

1-Amido-β-naphthol, from the reduction of 1-nitro- or nitroso-β-naphthol, or by the decomposition of β-naphthol orange, can be oxidised to β-naphtho-quinone. **1, 3-Amido-naphthol** decomposes at 185° (B. **28,** 1952). **1, 3-Amido-naphthol** decomposes at 185° (B. **28,** 1952). **2, 3-Amido-naphthol,** melting at 234°, is produced by the action of concentrated ammonia at 135°–140° (B. **27,** 763) upon 2, 3-dioxy-naphthalene.

1, 6-Amido-naphthol, m.p. 186°, obtained from β-naphthol, 2, 6- and 2, 8-naphthol-sulphonic acids. **1, 5-Amido-naphthol,** from α-naphthol and 1, 5-naphthol-sulphonic acid on fusion with Na amide. **1, 8-(peri-)-Amido-naphthol,** m.p. 96°, from 1, 8-naphthylamine-sulphonic acid by fusion with potash (B. **39,** 3331; **42,** 4748). **1, 7-Amido-naphthol,** m.p. 165°, see B. **42,** 350.

Azo-naphthols.—The naphthols can be readily combined with all diazo-compounds to azo-derivatives. The α-naphthols add the diazo-group as easily to the para-(4-) as to the ortho-(2-) position. However, the p-position is preferred, and it is only when this is occupied that the o-position is assumed (B. **29,** 2945; **30,** 50; **31,** 2156). The final products are o, p-dis-azo-compounds. With the β-naphthols the diazo-group attaches itself only to the α-position referred to the OH group.

From α-naphthol we obtain in the first instance **1, 4-Naphthol-azo-benzol** $(OH)[1]C_{10}H_6[4]N : NC_6H_5$ and **1-naphthol-2, 4-dis-azo-benzol** $(OH)[1]C_{10}H_5[2, 4](N : NC_6H_5)_2$; from β-naphthol, **2-naphthol-1-azo-benzol** $(OH)[2]C_{10}H_6[1]N : NC_6H_5$.

These same compounds are also obtained by the action of phenyl-hydrazin upon the *naphtho-quinones.* α-Naphtho-quinone-phenyl-hydrazone is identical with 1-naphthol-4-azo-benzene. β-Naphtho-quinone and phenyl-hydrazin form a compound which probably is **1-naphthol-2-azo-benzene,** melting at 128°, which cannot be directly made from α-naphthol, because it is converted by diazo-benzene chloride into 1-naphthol-2, 4-dis-azo-benzene.

In spite of this formation, the azo-naphthols, like the azo-phenols, must be regarded as true oxy-azo-compounds. In 1-naphthol-2-azo-benzol, the tendency towards the azo-structure is so strong that the acyl-phenyl-hydrazones immediately transpose into the isomeric O-acyl-compounds, which are also obtained direct by acylation of the **1-naphthol-2-azo-benzol** (A. **359,** 353):

$$C_{10}H_6\begin{cases}O\\ N.N(Ac)C_6H_5\end{cases} \longrightarrow C_{10}H_6\begin{cases}OAc\\ N : NC_6H_5\end{cases}.$$

The naphthol-azo-dyes are of great importance in the colour industry. They are prepared almost exclusively in the form of their sulpho-acids, which are formed (1) by the union of the naphthols with diazo-sulphonic acids—*e.g.* **α-naphthol orange** $OH[1]C_{10}H_6[4].N_2.C_6H_4.SO_3H$, **β-naphthol orange** $OH[2]C_{10}H_6[1]N_2C_6H_4SO_3H$, **roccellin** $OH[2]C_{10}H_6[1]N_2.C_{10}H_6.SO_3H$, **Bieberich scarlet** $OH[2]C_{10}H_6[1]N_2.C_6H_3(SO_3H)N_2.C_6H_4SO_3H$, forms α- and β-naphthols with diazo-benzene-sulphonic acid, diazo-naphthalene-sulphonic acid, and sulpho-benzene-azo-benzene-sulphonic acid; (2) by the combination of diazo-salts with naphthol-sulphonic acids. Cp. B. **29,** 2945, for the dye-stuffs obtained from naphthacetol and diazo-compounds.

Amido-naphthols, together with amines, are obtained by the reduction of azo-naphthols. The benzene-azo-p-naphthol ethers, when reduced with $SnCl_2$, yield *2-anilido-1, 4-amido-naphthol ethers* $C_{10}H_5(OR)(NH_2)(NHC_6H_5)$; the aniline residue enters consequently into the nucleus (B. **25,** 1013); cp. semidin rearrangement (p. 146).

(*d*) *Naphthol-sulphonic acids* have been made in great numbers and introduced into trade. In method of preparation and chemical behaviour they exhibit nothing new, when compared with the phenol-sulphonic acids. In the following paragraph, therefore, a table alone of the representatives of these groups which possess a technical value will be introduced: *

* Cp. Nietzki, *Organische Farbstoffe.*

α-Naphthol-mono-sulphonic acids :

$C_{10}H_6OH.SO_3H$

1	2	Schaeffer's α-acid, A. **152**, 293.
1	3	B. **26**, R. 31.
1	4	Neville and Winther's acid, B. **24**, 3157; **27**, 3458; A. **278**, 102.
1	5	L-acid, A. **247**, 343.
1	7	B. **22**, 993.
1	8	Schöllkopf's acid, A. **247**, 306; B. **23**, 3088.

β-Naphthol-mono-sulphonic acids :

$C_{10}H_6.OH.SO_3H$

2	6	Schaeffer's β-acid, A. **152**, 296.
2	8	*Crocein acid*, B. **22**, 453; **24**, R. 654.
2	5	γ-Mono-sulphonic acid, B. **22**, R. 336.
2	7	F- or δ-acid, B. **20**, 1426; **22**, 724.

α-Naphthol-disulphonic acids :

$C_{10}H_5OH.SO_3H.SO_3H$

1	2	4	Disulphonic acid for Martius' yellow.
1	2	7	B. **25**, 1400.
1	3	8	ε-Disulphonic acid, B. **22**, 3227.
1	4	6	D R.P. 41,957.
1	4	7	B. **24**, R. 709; **29**, 38.
1	4	3	Disulphonic acid, S, B. **23**, 3090.

β-Naphthol-disulphonic acids :

$C_{10}H_5OH.SO_3H.SO_3H$

2	3	6	**R-acid**, B. **22**, 396.
2	3	7	δ-Disulphonic acid, B. **20**, 2906.
2	4	8	Disulphonic acid, C, B. **26**, R. 259.
2	6	8	**G-acid**, B. **24**, R. 707.

α-Naphthol-trisulphonic acids :

$C_{10}H_4OH.SO_3H.SO_3H.SO_3H$

1	2	4	7	Sulphonic acid for *naphthol yellow* p. (401).
1	3	6	8	Sulphonic acid for *Chromotrope*, B. **24**, R. 485.

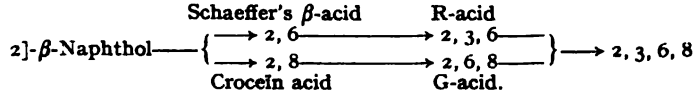
β-Naphthol-trisulphonic acids :

$C_{10}H_4OH.SO_3H.SO_3H.SO_3H$

2	3	6	8	B. **16**, 462.

(Consult B. **27**, 1207, 1209, for other β-naphthol-trisulphonic acids.)

It is the acid of Neville and Winther—of all these acids—which is principally used in the making of azo-dyes. It corresponds to naphthionic acid. It is obtained in its present state by the action of concentrated sulphuric acid upon α-naphthyl carbonate. The R-acid and G-acid also meet with application. They unite with benzene and naphthalene diazo-salts to form a series of *Ponceau-* and *Bordeaux-*dyes of the most varying hues. The most important sulphonic acids of β-naphthol are produced together or one after the other in the sulphonation of β-naphthol in the manner represented in the following diagram :



The naphthol-sulphonic acids containing an OH and SO_3H group in the 1, 8- or peri-position give rise to anhydrides having a lactone nature; these are the *sultones* (cp. sultames).

Naphtho-sultone $C_{10}H_6\begin{cases}[1]O\\ |\\ [8]SO_2\end{cases}$, melting at 154° and boiling above 360°, is formed by decomposing the diazo-derivative of peri-naphthylamine-sulphonic acid. The sultone dissolves in hot alkalies, forming salts of peri-naphthol-sulphonic acid. Sultones have also been obtained from 1, 3, 8- and 1, 4, 8-naphthol-di- and 1, 3, 6, 8-trisulphonic acids.

Amido-naphthol-sulphonic Acids are produced in the decomposition, by reduction, of the azo-derivatives of naphthol-sulphonic acids, and from nitroso-naphthols by reduction and sulphonation, both of which processes can be worked in common if the nitroso-naphthols be treated with sulphurous acid (B. **27,** 23, 3050). In this way 1, 2-nitroso-naphthol yields **1, 2, 4-amido-naphthol-sulphonic acid** $C_{10}H_5[1]NH_2[2]OH[4]SO_3H$. The isomeric 2, 1, 4-acid $C_{10}H_5[1]OH[2]NH_2[4]SO_3H$ produces, even when oxidised in the air, *imido-oxy-naphthalene-sulphonic acid* $SO_3H.C_{10}H_5\begin{cases}O\\ |\\ NH\end{cases}$. This dye is black-violet in colour, and is fast to light and alkalies (B. **25,** 1400; **26,** 1279). The 2, 1, 6-*acid* $C_{10}H_5[1]OH[2]NH_2[6]SO_3H$ is used as a photographic developer under the name of *eikonogen*. Important dyes, from the technical point of view, are 2-amido-8-naphthol-6-sulphonic acids G (B. **25,** R. 830; **29,** 2267) and 1-amido-8-naphthol-3, 6-disulphonic acid H (B. **26,** R. 460, 917). Also 2-amido-5-naphthol-7-sulphonic acid (C. 1907, II. 1467), and some 1, 8-amido-naphthol-sulphonic acids for black wool dyes; 2-amido-5-naphthol-1-sulphonic acid (C. 1911, I. 1263). Further amido-naphthol-sulphonic acids, see *J. pr. Ch.* 2, **80,** 201.

Dioxy-naphthalenes.—Nine of the ten possible isomerides are known. The hydro-naphtho-quinones resulting from the reduction of the naphtho-quinones are worthy of mention:

β-Hydro-naphtho-quinone $C_{10}H_6[1, 2](OH)_2$, melting at 60°, separates when a solution of β-naphtho-quinone is boiled with sulphurous acid. It is strongly corrosive. It dissolves in the alkalies with a yellow colour, which becomes an intense green upon exposure.

α-Hydro-naphtho-quinone $C_{10}H_6[1, 4](OH)_2$, melting at 173°, is obtained from α-naphtho-quinone on boiling with hydriodic acid and phosphorus, or with zinc and hydrochloric acid. Chromic acid readily oxidises it to α-naphtho-quinone.

2, 6-Dioxy-naphthalene, m.p. 218°, from Schaeffer's β-naphthol-sulphonic acid by fusion with potash, passes into the 2, 6- or amphi-naphtho-quinone on oxidation with PbO_2. From this it is recovered by reduction with dilute HI (B. **40,** 1410).

2, 3-Dioxy-naphthalene melts at 216° (B. **27,** 762). Its mono-methyl ether, m.p. 108°, acts physiologically like guaiacol (B. **27,** 762; C. 1902, II. 554, 744). Also cp. A. **247,** 356; B. **23,** 519, etc.

1, 3-Dioxy-naphthalene, *naphtho-resorcinol*, melting at 124°, is obtained from 1, 3, 4-amido-naphthol-sulphonic acid. It yields o-toluic acid when fused with caustic potash (see B. **29,** 1611).

2-Phenyl-1, 3-dioxy-naphthalene, melting at 166°, is made by the action of concentrated sulphuric acid upon α, γ-diphenyl-aceto-acetic ester (p. 653). It absorbs oxygen and changes readily to phenyl-hydroxy-α-naphtho-quinone. *1, 7-Dioxy-naphthalene* melts at 175°; see B. **29,** 40; *2, 7-dioxy-naphthalene*, see B. **30,** 1119.

1, 8-(Peri-) dioxy-naphthalene, m.p. 140°, from naphtho-sultone by fusion with potash (A. **247,** 356). The 1, 8-dioxy-naphthalene-3, 6-disulphonic acid (" chromo-tropic acid ") is obtained by fusing the naphthol-trisulphonic acid with potash. It is a component of valuable o-oxy-azo-dyes (B. **31,** 2156).

Trioxy-naphthalenes.—Two trioxy-naphthalenes, α- and **β-hydro-juglones,** occur in green walnut shells of *Juglans regia* (B. **18,** 463, 2567). **α-Hydro-juglone** $C_{10}H_5[1, 4, 5](OH)_3$, melting at 169°, is produced by the reduction of juglone. In the air it rapidly oxidises to juglone. If it be distilled it changes to **β-hydro-juglone,** melting at 97°, which does not yield juglone upon oxidation. It reverts again to α-hydro-juglone when boiled with dilute alcoholic hydrochloric acid.

1, 2, 4-Trioxy-naphthalene, m.p. 154°, is obtained as a triacetate, m.p. 134°, by the action of acetic-anhydride-sulphuric acid upon α- and β-naphtho-quinone (A. **311,** 345). **1, 3, 6-Trioxy-naphthalene,** m.p. 95°, see B. **38,** 3945.

1, 2, 5, 6-Tetraoxy-naphthalene, m.p. 154°, by reduction of naphthazarin (see below) (B. **28,** R. 543). Reduction of iso-naphthazarin gives **1, 2, 3, 4-tetraoxy-naphthalene,** and on further reduction a **1, 2, 3-trioxy-naphthalene,** *naphtho-pyrogallol* (A. **307,** 16).

Thio-naphthols have been prepared by the reduction of the chlorides of naphthalene-sulphonic acids or from diazo-naphthalenes. **Thio-naphthol,** *naphthyl-mercaptan* $C_{10}H_7.SH$; the α-form is liquid and boils at 286°. The β-variety melts at 81° and boils at 286° (B. **22,** 821; **23,** R. 327). **Phenyl-β-naphthyl sulphide,** melting at 51° (B. **24,** 2266), is formed when the *lead salt* $(C_{10}H_7\text{-}\beta\text{-}S)_2Pb$ is heated, together with bromo-benzene. Different **dinaphthyl sulphides** have been prepared by heating the naphthyl-lead mercaptides. Other methods have been employed in making them (B. **26,** 2816). Sulphur chloride and β-naphthol yield **dioxy-dinaphthyl sulphide** $S(C_{10}H_6.OH)_2$, melting at 211°. This can be readily oxidised to a *dehydro*-compound $S\langle{}^{C_{10}H_6O}_{C_{10}H_6O}\rangle$ (B. **27,** 2993; **28,** 114) (cp. quinones with two nuclei).

Naphthalene disulphydrates $C_{10}H_6(SH)_2$; see B. **25,** 2735.

10. *Quinones.*—On the basis of the diketone formula for the quinones, six different naphtho-quinones are theoretically conceivable, comprising three single-nucleus quinones, corresponding to the benzo-quinones, and three double-nucleus quinones :

α-Naphtho-quinone | β-Naphtho-quinone | 2, 3-Naphtho-quinone | 1, 5-Naphtho-quinone | Amphi-naphtho-quinone | 1, 7-Naphtho-quinone.

Out of these, only the 1, 4-(α)-, the 1, 2-(β)- and the 2, 6-(amphi-) naphtho-quinone, and a derivative of the 2, 3-naphtho-quinone, have hitherto been prepared.

α-Naphtho-quinone $O=[1]C_{10}H_6[4]=O$, melting at 125°, crystallises from alcohol in yellow plates, subliming under 100°. It possesses the usual quinone odour, and is very volatile in a current of steam. It is

formed (1) by oxidising naphthalene in glacial acetic acid solution with chromic acid; (2) in the oxidation of 1, 4-diamido- or 1, 4-dioxy-naphthalene, 1, 4-amido-naphthol (A. **286**, 70), α-naphthylamine, etc., with sodium bichromate and sulphuric acid (B. **20**, 2283); and (3) when benzene-azo-naphthol is treated in the cold with PbO_2 and sulphuric acid it is decomposed into diazo-benzene sulphate and α-naphtho-quinone (B. **24**, R. 733).

Nitric acid oxidises α-naphtho-quinone to phthalic acid, while α-hydro-naphtho-quinone is produced in its reduction. See the nitrogen-quinone derivatives for its phenyl-hydrazin and hydroxyl-amine derivatives.

Substituted α-Naphtho-quinones.—α-Naphtho-quinone takes up two atoms of chlorine or bromine; the addition products readily part with hydrochloric and hydrobromic acids and become **β-chloro-** and **β-bromo-α-naphtho-quinones,** melting at 117° and 130°. **2, 3-Dichloro-** and **2, 3-dibromo-naphtho-quinone,** m.p. 189° and 218°.

In these halogen quinones, as in the αβ-dihalogen indones, the halogen atoms are easily replaced by other groups. Thus, from the dihalogen-α-naphtho-quinones we obtain with sodium-aceto-acetic ester and sodium-malonic ester, with intermediate beautiful red and blue colorations, such compounds as

$C_6H_4\langle^{CO—CBr}_{CO—C.CH(CO_2C_2H_5)_2}$, m.p. 102°, bromo-α-naphtho-quinone-malonic ester.

$C_6H_4\langle^{CO—C.CH(CO_2C_2H_5)_2}_{CO—C.CH(CO_2C_2H_5)_2}$, m.p. 98°, α-naphtho-quinone-dimalonic ester.

$C_6H_4\langle^{CO—CCl}_{CO—C.CH(COCH_3)CO_2C_2H_5}$, m.p. 107°, chloro-α-naphtho-quinone-aceto-acetic ester.

From these compounds many derivatives of the naphtho-quinone series can be obtained by further transformations (B. **38**, 566, 2402; **34**, 1543). Condensation of 2, 3-dichloro-α-naphtho-quinone with resorcin or orcin and sodium ethylate produces derivatives of phenylene-naphthylene oxide $C_6H_4\langle^{CO.C}_{CO\ C.O}\rangle C_6H_3OH$, which are closely related to some decomposition products of brasilin, the so-called *brasanes* (B. **32**, 924; **41**, 2373).

Hypochlorous acid converts α-naphtho-quinone into *diketo-tetra-hydro-naphthylene oxide* $C_6H_4\langle^{CO—CH}_{CO—CH}\rangle O$, which, by the breaking down of the ethylene-oxide union, readily takes up the elements of water, hydrogen chloride, and $NH_2C_6H_5$. The primary addition products sustain the most varied transpositions with great readiness, and form: *oxy-naphtho-quinone, chloroxy-naphtho-quinone, anilido-oxy-naphtho-quinone, oxy-naphtho-quinone-anile,* and other bodies; cp. B. **25**, 3599.

Amido-derivatives.—Alkyl- or alphyl-amido-naphtho-quinones are produced on heating primary amines together with α-naphtho-quinone: **2-anilido-α-naphtho-quinone** $C_{10}H_5O_2[2]NH.C_6H_5$ consists of red needles, melting at 191°. **2-Amido-α-naphtho-quinone,** melting at 203°, is formed together with the isomeric oxy-α-naphtho-quinone-imide on boiling amido-α-naphtho-quinone-imide with water (B. **27**, 3337; B. **28**, 348).

Oxy-naphtho-quinones.—**2-Oxy-α-naphtho-quinone,** ***naphthalic acid*** $C_{10}H_5O_2[2]OH$, melting at 188°, is produced when anilido-naphtho-quinone (see above) is boiled with dilute sodium hydroxide or oxy-naphtho-quinone-anile with alcohol and sulphuric acid. **β-Phenyl-β_1-oxy-α-naphtho-quinone,** melting at 147°, is prepared from β-phenyl-1, 3-dioxy-naphthalene by oxidising it in alkaline solution with air (A. **296,** 18). **Iodo-oxy-naphtho-quinone,** ***iodo-naphthalic acid*** $C_{10}H_4O_2[2]OH[3]I$, results from the iodation of naphthalic acid (B. **28,** 348). Dyes of the *paroxazine* and *paradiazine* series are easily made from the o-oxy- and o-amido-naphtho-quinone derivatives (cp. also the corresponding naphtho-quinone-aniles and o-diamines) (B. **28,** 353).

5-Oxy-α-naphtho-quinone, juglone, consists of yellow needles, melting with decomposition about 150°–155°. The best method to obtain it consists in oxidising α-hydro-juglone with ferric chloride. It may be synthetically prepared by oxidising (1, 5)-dioxy-naphthalene with chromic acid (B. **20,** 934). It dissolves in alkalies with a violet colour. Nitric acid converts it into dinitro-oxy-phthalic acid (*juglonic acid*) (B. **19,** 164).

Oxy-juglone, *dioxy-α-naphtho-quinone,* melting with decomposition at 220°, is produced by the oxidation of the alkaline solution of juglone on exposure to the air. An isomeric **5, 6-dioxy-α-naphtho-quinone,** *naphthalizarin* or **naphthazarin,** is formed on heating various α-dinitro-naphthalenes with concentrated sulphuric acid in the presence of reducing agents (B. **27,** 3462, R. 959; A. **286,** 26). It corresponds to alizarine, which may be imagined to have arisen from naphthazarin by the addition of a benzene nucleus. It is a valuable *mordant dye.*

Oxidation with MnO_2 and sulphuric acid yields the naphthazarin called **naphtho-purpurin,** 5, 7, 8-trioxy-α-naphtho-quinone (C. 1899, II. 1053).

Iso-naphthazarin is probably a 2, 3-**dioxy-α-naphtho-quinone.** It is produced from β-naphtho-quinone by the action of a little bleaching-lime as well as when 2, 3-oxy-anilido-α-naphtho-quinone (see above) is heated with bromine (B. **25,** 409, 3606).

Iso-naphthazarin, on reduction, gives tetra- and trioxy-naphthalene, and, on oxidation, tetra-keto-naphthalene $C_6H_4(CO)_4$, which partly regenerates iso-naphthazarin, and phenyl-glyoxal-o-carboxylic acid, with hydroxylamine or dioxime, m.p. 228°, which, on oxidation, yields dinitroso-α-naphtho-quinone $C_6H_4[C_4O_2(NO)_2]$(A. **307,** 1). Closely related to iso-naphthazarin is carminazarin, from oxidation of carminic acid. On **6, 7-Dioxy-α-naphtho-quinone,** see C. 1902, II. 744.

β-Naphtho-quinone $C_{10}H_6[1, 2]O_2$ is produced on oxidising β-amido-α-naphthol with ferric chloride (B. **17,** R. 531; **21,** 3472). It consists of red needles, which decompose at 115°–120°. It is distinguished from the para-quinones by being odourless and non-volatile. It closely resembles anthraquinone, and especially phenanthraquinone; like the latter, it must be considered an ortho-diketone $C_6H_4\langle^{CH:CH}_{CO.CO}$.

Like α-naphtho-quinone, it can add two atoms of chlorine and bromine, and by the elimination of halogen hydrides **chloro-** and **bromo-β-naphtho-quinones** are formed.

3, 4-Dichloro- and **dibromo-β-naphtho-quinone,** m.p. 91° and 173°; **β-naphtho-quinone-malonic ester** $C_6H_4[C_4O_2H.CH(COOR)_2]$, m.p. 108°.

3-Chloro-β-naphtho-quinone-aceto-acetic ester, m.p. 175°, see B. **32,** 264, 2412.

A little bleaching-lime converts β-naphtho-quinone into *iso-naphthazarin* (together with various other products, A. **286,** 59). This is a dioxy-α-naphtho-quinone. Such a rearrangement of 4-oxy- or 4-amido-β-naphtho-quinone derivatives into oxy-α-naphtho-quinone compounds is a phenomenon that has been frequently observed (cp. oxy-α-naphtho-quinone-anile). An excess of bleaching-lime will produce a rupture in the ring of β-naphtho-quinone and convert it into the lactone of o-phenyl-glycerol-carboxylic acid.

Similarly, **3-nitro-1, 2-naphtho-quinone,** melting at 158°, and obtained by the nitration of β-naphtho-quinone, is changed, on treating it with chlorine and water, into o-di-derivatives of benzene.

3, 4-Dichloro-1, 2-naphtho-quinone, on the contrary, is first rearranged by alkalies into dichlor-indene-oxy-carboxylic acid. Potassium permanganate oxidises β-naphtho-quinone to phthalic acid, while sulphurous acid reduces it to β-naphtho-hydroquinone, and hydriodic acid to β-naphthol (B. **26,** R. 586).

6-Bromo-4-chloro-1-methyl-2, 3-naphtho-quinone $C_{10}H_3[6]Br[4]Cl[1]CH_3[2, 3]O_2$, yellow prisms, decomposing at 220°, has been obtained from the lead salt of the corresponding 2, 3-dioxy-naphthalene by the action of iodine. It is odourless and non-volatile. Zinc dust and glacial acetic acid partly reduce it to the corresponding dioxy-naphthalene. With o-phenylene-diamine it combines like the ortho-diketones to form a derivative of naphtho-phenazene (B. **42,** 3375).

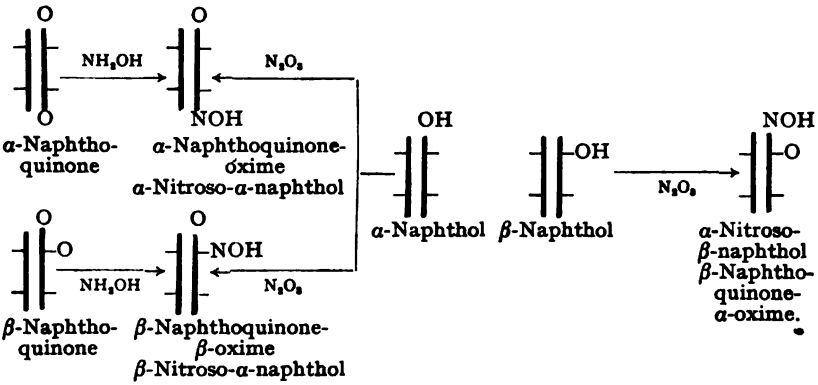
2, 6-(amphi-) Naphtho-quinone $C_{10}H_6[2, 6]O_2$, reddish-yellow crystals, decomposed at 130°–135°, is formed by the oxidation of 2, 6-dioxy-naphthalene with PbO_2 in benzene solution. It is odourless and non-volatile, and distinguished by its strong oxidising action. Dilute HI reduces it to 2, 6-dioxy-naphthalene, with which it unites molecularly to a blue green *quin-hydrone,* decomposing at 124°. More stable than amphi-naphtho-quinone itself is its dichloro-substitution product, **1, 5-dichloro-amphi-naphtho-quinone,** m.p. 206°, obtained similarly from 1, 5-dichloro-2, 6-dioxy-naphthalene (B. **40,** 1406, 3971).

Nitrogen Derivatives of the Naphtho-quinones.

1. *Naphtho-quinone-phenyl-hydrazones.* — Unlike the benzene quinone, both the α- and β-naphtho-quinones unite with phenyl-hydrazin and form *phenyl-hydrazones* (B. **28,** 2414). The quinone-phenyl-hydrazones are identical with the benzol-azo-naphthols (B. **32,** 3100). The results of the action of unsym. acyl-phenyl-hydrazins upon β-naphtho-quinone must probably be regarded as O-acylated azo-naphthols (B. **40,** 2153; A. **359,** 353). On the other hand, α-naphtho-quinone with unsym. benzoyl- and methyl-phenyl-hydrazin have yielded products $C_{10}H_6\langle^{NN(COC_6H_5)C_6H_5}_{O}$ and $C_{10}H_6\langle^{NN(CH_3)C_6H_5}_{O}$, differing from those obtained by methylating and benzoylating 1, 4-naphthol-azo-benzol $C_{10}H_6\langle^{N:NC_6H_5}_{OCOC_6H_5}$ and $C_{10}H_6\langle^{N:NC_6H_5}_{OCH_3}$ (C. 1900, I. 31).

2. *Nitroso-naphthols or Naphtho-quinoximes.*—These are produced when the alcoholic solutions of the α- and β-naphtho-quinones are

boiled with hydroxylamine hydrochloride, and by the action of nitrous acid upon the naphthols; hence they can be regarded as nitroso-naphthols $C_{10}H_6(O)(NOH)$ or $C_{10}H_6(OH)(NO)$ (cp. nitroso-phenols, p. 198). Three isomeric bodies are formed; their relation is expressed by the following diagram:



The three isomerides are weak acids. Oxidation converts them into the corresponding nitro-naphthols.

α-Nitroso-α-naphthol, α-naphtho-quinone-oxime, melting at 190°, and **β-nitroso-α-naphthol, β-naphtho-quinone-β-oxime,** melting at 152°, are colourless compounds. β-Naphtho-quinone-oxime is best made from 1-oxy-2-naphthoic acid with nitrous acid, when the carboxyl group is split off (B. **26,** 1280). **α-Nitroso-β-naphthol,** *β-naphtho-quinone-α-oxime,* consisting of yellow-brown prisms, melting at 106°, precipitates different metals from their salts, and may be used to separate nickel from cobalt, iron from aluminium, and for the determination of copper (B. **18,** 2728; **20,** 283). *Naphthol green* (B. **24,** 3741), a wool dye, is the iron salt of **α-nitroso-β-naphthol-sulphonic acid** $C_{10}H_5(SO_3H)O(NOH)$, obtained by the action of nitrous acid upon Schaeffer's β-naphthol-sulphonic acid. Consult B. **30,** 187, for the product obtained in the action of NO_2 vapours upon Schaeffer's β-acid.

The *ethers* of the nitroso-naphthols, derived from the silver salts with methyl iodide and partly from the quinones with alkyl-hydroxyl-amines, are reduced to amido-naphthols by tin chloride (B. **18,** 715, 2225), a proof of the " oxime formula " of the nitroso-naphthols.

α-Naphtho-quinone-dioxime $C_{10}H_6$-1, 4-$\begin{matrix}\diagup\!\!\diagdown\text{N.OH}\\ \diagdown\!\!\diagup\text{N.OH}\end{matrix}$ is formed from α-nitroso-α-naphthol with hydroxylamine hydrochloride. It melts at 207° (B. **21,** 433).

β-Naphtho-quinone-dioxime $C_{10}H_6$-1, 2-$\begin{matrix}\diagup\!\!\diagdown\text{N.OH}\\ \diagdown\!\!\diagup\text{N.OH}\end{matrix}$ is derived from β-nitroso-α-naphthol and from α-nitroso-β-naphthol by the action of hydroxylamine hydrochloride (B. **17,** 2064, 2582). It melts at 149°. After the manner of the glyoximes it forms the *anhydride* $C_{10}H_6\begin{cases}[1]\text{N}\\ [2]\text{N}\end{cases}\!\!>\!\text{O}$, melting at 78°, when digested with alkalies. This compound may also be designated *naphtho-furazane.* The reduction of the dioximes gives rise to naphthylene-diamine.

3. *Naphtho-quinone Chlorimides.*—These are made from amido-

naphthols, and the dichlorimides from the naphthylene diamines with a bleaching-lime solution (B. **27,** 238). They resemble the benzoquinone chlorimides, but do not exhibit the same dyestuff condensations as the former (B. **27,** 242).

α-Naphtho-quinone-chlorimide $C_{10}H_6[1,4](NCl)O$ melts at 109°.

α-Naphtho-quinone-dichlorimide, $C_{10}H_6[1,4](NCl)_2$ melts at 137°.

β-Naphtho-quinone-α-chlorimide, melting at 87°, and **β-naphtho-quinone-β-chlorimide,** decomposing at 98°, are derived from 2, 1- and 1, 2-amido-naphthols; they yield β, α- and α, β-nitroso-naphthols with hydroxylamine. **β-Naphtho-quinone-dichlorimide** melts at 105°.

4. *Naphtho-quinone-imines and Aniles.*—The indo-phenol and indo-aniline dyes of the naphthalene series belong to this group—*e.g.* **α-naphthol blue** or **indo-phenol** $C_{10}H_6[1]O[4]N.C_6H_4N(CH_3)_2$—which results when naphthol interacts with dimethyl-p-phenylene-diamine or nitroso-dimethyl-aniline. The simple α-naphtho-quinone-imide is not known. **2-Amido-1, 4-naphtho-quinone-imine,** *di-imido-naphthol* $C_{10}H_5[2]NH_2[1]O[4]NH$ (A. **154,** 303) is produced in the oxidation of 1-oxy-2, 4-diamido-naphthalene. Boiling water changes di-imido-naphthol to **2-oxy-1, 4-naphtho-quinone-imine,** melting at 195° (B. **23,** 2454); aniline to **2-amido-1, 4-naphtho-quinone-anile** $C_{10}H_5[2]NHC_6H_5[1]O[4]NC_6H_5$, melting at 187° (B. **18,** 123; **21,** 391, 676); and further to **2-anilido-1, 4-naphtho-quinone-anile** (C. 1910, I. 926); with hydroxylamine an **oxy-naphtho-quinone-oxime,** which consists of two modifications, red and yellow, which can be changed one into the other (B. **29,** 1415).

α-Naphtho-quinone-anile $C_{10}H_6[1]O[4]NC_6H_5$, red columns, m.p. 100°, and **β-naphtho-quinone-anile** $C_{10}H_6[1]O[2]NC_6H_5$, m.p. 103°, dark-green needles, are formed by alkaline condensation of nitroso-benzol with α- and β-naphthol respectively (B. **39,** 1035).

2-Oxy-1, 4-naphtho-quinone-anile, melting at 240° with decomposition, is produced by the action of aniline in the cold upon β-naphtho-quinone-4-sulphonic acid, the oxidation product of 1, 2-amido-naphthol-4-sulphonic acid. This is an instance of the rearrangement of a β- into an α-naphtho-quinone derivative. The p-diamines react in a manner similar to aniline, so that in this way hydroxyl-indaniline dyes (see above) can be obtained (B. **27,** 25, 3050).

α-Naphtho-quinone-phenyl-di-imide $C_{10}H_6(NH)(NC_6H_5)$, melting at 129°, is formed upon oxidising p-amido-naphthyl-phenyl-amine with mercuric oxide (A. **286,** 186).

β-Naphtho-quinone-imides, also called *imido-oxy-* or *imido-ketone naphthalenes, e.g.* $C_{10}H_6$-1, 2-O(NH), are produced when the alkaline solutions of 1, 2-amido-naphthols are oxidised with air.

11. Alcohols of the Naphthalene Series and their Oxidation Products.

A. *Alcohols.*—**Naphtho-benzyl alcohols,** *naphthyl-carbinols* $C_{10}H_7.CH_2.OH$, the α- melting at 60° and boiling at 301°, and the β- melting at 80°, result when their amines are treated with nitrous acid (B. **21,** 257). The **naphtho-benzyl chlorides** $C_{10}H_7CH_2Cl$, the α- boiling at 178° (25 mm.) and the β- melting at 47°, are formed when chlorine acts upon the two methyl-naphthalenes at a boiling temperature (B. **24,** 3928).

Naphtho-benzyl-amines *menaphthyl-amines* $C_{10}H_7.CH_2.NH_2$, the α-boiling at 292° and the β- melting at 60°, have been made by the reduction of the corresponding naphthoic acid thiamides, as well as of the naphtho-nitriles.

α- and **β-Naphthyl-nitro-methane** $C_{10}H_7.CH_2NO_2$, m.p. 73° and 72°, show isomeric phenomena similar to those of phthalyl-nitro-methane. They have been obtained from the naphthyl-aceto-nitriles by the action of ethyl nitrate and sodium ethylate and splitting up of the resulting nitro-aceto-nitriles by boiling with soda (B. **38,** 508).

α-Naphthyl-dimethyl-carbinol $C_{10}H_7[α]C(OH)(CH_3)_2$, m.p. 80°, from α-naphthyl-methyl-ketone with CH_3MgI, and from α-naphthyl-magnesium bromide and acetone. **α-Naphthyl-phenyl-carbinol** $C_{10}H_7CH(OH)C_6H_5$, m.p. 86°, and **α-naphthyl-diphenyl-carbinol** $C_{10}H_7C(OH)(C_6H_5)_2$, m.p. 133°, from α-naphthyl-magnesium bromide, with benzaldehyde and benzo-phenone respectively (B. **37,** 625, 2755). Other naphthyl-carbinols, see C. 1910, I. 1144.

B. *Aldehydes, Ketones.*—When the naphthyl-methyl alcohols are oxidised, the products are :

α-Naphthaldehyde $C_{10}H_7.CHO$, boiling at 291°, and **β-naphthaldehyde,** melting at 59° (B. **20,** 1115 ; **22,** 2148 ; **44,** 447). **α-Naphthyl-acetaldehyde** $C_{10}H_7.CH_2.CHO$, b.p.$_{18}$ 163°–166°, from α-vinyl-naphthalene with HgO and I (C. 1908, II. 1780).

α- and **β-Naphthyl-methyl-acetaldehyde** $C_{10}H_7CH(CH_3)CHO$, b.p.$_4$ 132° and m.p. 53°, by condensation of α- and β-naphthyl-methyl-ketone with chloro-acetic ester and sodium ethylate, the resulting glycide esters being saponified with loss of CO_2 (C. 1908, I. 644). The α-compound has also been obtained by the action of HgO and I upon α-propenyl-naphthalene (C. 1908, II. 1780).

α-Naphthyl-methyl-ketone, *aceto-naphthone* $C_{10}H_7.CO.CH_3$ is derived from naphthalene and acetyl chloride by means of aluminium chloride. It melts at 34° and boils at about 295°. Its chloride splits off hydrogen chloride and becomes *α-naphthyl-acetylene* $C_{10}H_7.C : CH$. Potassium permanganate oxidises the ketone to α-naphthyl-glyoxylic acid $C_{10}H_7CO.COOH$, melting at 113°, which is also formed by the saponification of naphthol cyanide obtained from α-naphthoyl chloride.

α-Naphthoyl-o-benzoic acid $C_{10}H_7COC_6H_4COOH$, m.p. 173°, from phthalic anhydride, naphthalene, and $AlCl_3$ (B. **33,** 448). The action of Na amide and alkylene iodide produces trialkyl-aceto-naphthones, corresponding to aceto-phenones (C. 1910, II. 83). Other acyl-naphthyl-ketones, see C. 1908, II. 948. **Phenyl-naphthyl-ketones** $C_{10}H_7COC_6H_5$, see C. 1908, II. 1357.

1, 4- and **2, 1-Naphthol-aldehyde** $C_{10}H_6(OH)CHO$, m.p. 181° and 81°, are best obtained by Gattermann's method in the form of aldimines (B. **32,** 284 ; C. 1901, I. 1010). **1, 2-naphthol-aldehyde,** m.p. 59°, has been obtained by the condensation of α-naphthol with isatin chloride (M. **29,** 382 ; **30,** 277). From naphthol-sulphonic acids, naphthol-aldehyde-sulphonic acids are obtained by Reimer's aldehyde synthesis (C. 1898, II. 799).

1-Naphthol-3-methyl-ketone $C_{10}H_6[1](OH)[3](CO.CH_3)$, melting at 174°, is formed from β-benzal-lævulinic acid by condensation (B. **24,** 3201). See B. **28,** 1946, for **1, 2-naphthol-methyl-ketone.**

Peri-dioxy-naphthyl-ketones $(HO)_2[1, 8]C_{10}H_5COR$, from peri-dioxy-

naphthalene with carboxylic acids, and zinc chloride, are lac-forming mordant dyes (C. 1901, II. 1287).

C. *Naphthalene-monocarboxylic Acids.*—**α-Naphthoic acid** $C_{10}H_7$-α-CO_2H, melting at 160°, is derived from α-naphtho-nitrile by saponification (B. **20,** 242 ; **21,** R. 834) ; by fusing α-naphthalene-sulphonic acid with sodium formate ; by the action of sodium on a mixture of α-bromo-naphthalene and chloro-carbonic ester ; and from naphthalene, urea chloride, and aluminium chloride (B. **23,** 1190). **β-Naphthoic acid,** melting at 182°, is formed from β-naphtho-nitrile (B. **24,** R. 725), as well as by the oxidation of β-alkyl-naphthalenes (B. **17,** 1527 ; **21,** R. 355). Both acids are decomposed when heated with baryta into CO_2 and naphthalene.

Homologous Naphthalene-carboxylic Acids.—**α-Naphthyl-acetic acid** $C_{10}H_7$-α-CH_2.COOH, melting at 131°, has been made by the reduction of α-naphthyl-glyoxylic acid, while the *β-acid*, melting at 139°, has been prepared by means of the cyanide from β-naphtho-benzyl chloride (B. **29,** 2373).

α- and **β-Naphthyl-acrylic acids** $C_{10}H_7$.CH : CHCOOH, m.p. 205° and 196° respectively, are found by Perkin's synthesis from the naphthaldehydes with Na acetate and acetic anhydride. With Na propionate, propionyl-naphthalene is mostly obtained, with loss of CO_2 (C. 1897, II. 800). α- and **β-Naphtho-cumarin** $C_{10}H_6\begin{cases}CH:CH\\ O—CO\end{cases}$, m.p. 141° and 118°, and their alkylated derivatives, have been obtained by the general cumarin methods from malic acid, aceto-acetic ester, etc. with H_2SO_4, and from the naphthaldehydes by Perkin's synthesis (B. **36,** 1966 ; **37,** 4484 ; M. **30,** 280).

β-Phenyl- and **β-naphthyl-α-naphthoic acids** are the *chrysenic* and *picenic* acids (see Chrysene and Picene).

Substituted Naphthoic Acids.—The nitration of α-naphthoic acid produces **1, 5-** and **1, 8-nitro-naphthoic acids,** melting at 239° and 275° respectively. Boiling nitric acid converts them into 1, 5-(α)- and 1, 8-(β-) dinitro-naphthalene. **1, 4-Nitro-naphthoic acid,** melting at 220°, results upon saponifying the nitrile, which is formed on treating the diazo-derivative of 1, 4-nitro-naphthyl-amine with potassium cuprous cyanide.

Ferrous sulphate and ammonia reduce the 1, 5-acid to a stable **amido-naphthoic acid (1, 5)-,** melting at 212° (B. **19,** 1981), whereas the same reagents reduce the 1, 8-acid to (1, 8)- or **peri-amido-naphthoic acid,** which, when free, passes like the 1, 8-amido-sulphonic acids quite readily into its inner anhydride, **naphtho-styril** $C_{10}H_6\begin{cases}[1]CO\\ [8]NH\end{cases}$, melting at 179° (B. **19,** 1131). **1, 4-Amido-naphthoic acid** melts at 177° (B. **28,** 1842).

See B. **24,** R. 637, for the **nitro-β-naphthoic acids. 2, 8-Amido-naphthoic acid,** melting at 214°, results upon treating the corresponding oxy-naphthoic acid with ammonia (B. **28,** 3089). Further nitro- and amido-naphthoic acids, see C. 1899, I. 288. **1, 3-** and **1, 4-Diamido-β-naphthoic acids,** m.p. 85° and 185°, decompose into CO_2 and 1, 3- or 1, 4-naphthylene-diamine. Their esters have been obtained by nuclear synthesis (C. 1907, II. 68, 539).

Oxy-naphthoic acids, naphthol-carboxylic acids, containing the OH-

and COOH-groups in the ortho-position, are prepared like the ortho-phenol-carboxylic acids—*i.e.* by heating the sodium naphtholates with CO_2 under pressure.

1, 2-(α-) Naphthol-carboxylic acid $C_{10}H_6[1](OH)[2](COOH)$, melting at 186°, is formed from α-naphthol and from β-naphthol-sodium with carbon dioxide and pressure at 120°–145°; **2, 1-(β)-naphthol-carboxylic acid,** melting with decomposition at 156°, is similarly produced; while if β-naphthol-sodium be heated more strongly, 200°–250°, in a current of carbon dioxide, the product will be *2, 3-naphthol-carboxylic acid,* melting at 216°. The 2, 1-(β)-naphthol-carboxylic acid is distinguished by the easy mobility of its carboxyl group. Heated alone, or when boiled with water, it changes to β-naphthol; nitrous acid converts it into α-nitroso-β-naphthol, and diazo-benzene salts into benzene-azo-β-naphthol, etc. The 2, 3-acid, on the other hand, is very stable, and resembles salicylic acid. Because of its striking and remarkable yellow colour the formula of a *keto-dihydro-naphthoic acid* $C_6H_4\begin{cases}CH_2—CO\\ CH=C.COOH\end{cases}$ has been proposed for this acid. The behaviour of the acid toward phenyl-hydrazin supports this view: it is very probable that at first a hydrazin is produced, which subsequently, owing to indol condensation, forms a pheno-naphtho-carbazol-carboxylic acid (B. **29,** 265; cp. also **M. 31,** 917). With thionyl chloride, α- and β-naphthol-carboxylic acids yield the corresponding chlorides (C. 1901, II. 1119). The 2, 3-naphthol-carboxylic acid with PCl_5 gives colourless **2-chloro-3-naphthoic acid chloride,** m.p. 56°, b.p.$_{160}$ 248° (B. **34,** 4158).

From 1, 2-naphthoic acid chloride and acetyl-2, 3-naphthoic acid chloride, transposition with sodium-malonic ester yields **β-oxy- 1, 2- and 2, 3-naphtho-cumarin-naphtho-tetronic acid** $C_{10}H_6\begin{cases}C(OH):CH\\ O——CO\end{cases}$, m.p. 258° and 240° (A. **367,** 253; **368,** 43).

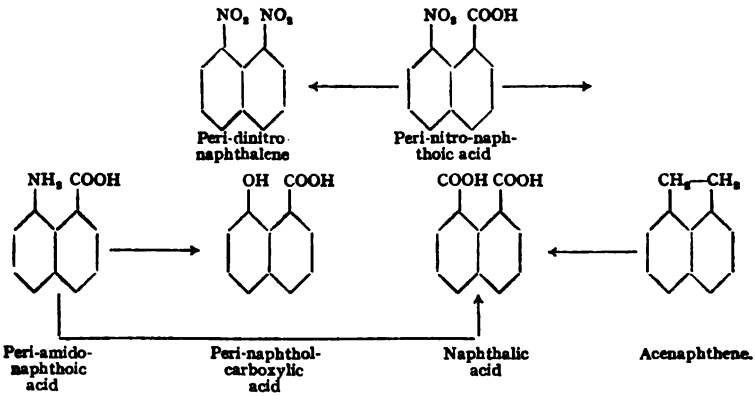
Naphtho-xanthones $C_{10}H_6\langle\begin{matrix}O\\CO\end{matrix}\rangle C_{10}H_6$ (B. **25,** 1642) are produced when the three o-naphthol-carboxylic acids are heated with acetic anhydride.

(1, 8)- or peri-naphthol-carboxylic acid is derived from (1, 8)-amido-naphthoic acid by means of the diazo-compound. It breaks down into water and its *γ-lactone* $C_{10}H_6\begin{cases}[1]O\\[8]CO\end{cases}\rangle$, melting at 169°.

2, 3-Oxy-naphthoic acid and diazo-benzene chloride yields a mixed azo-compound. Reduction converts this into **1, 2, 3-amido-oxy-naphthoic acid,** which, on boiling with sulphuric acid, becomes **1, 2, 3-dioxy-naphthoic acid.** This can also be obtained from β-naphtho-hydroquinone and carbon dioxide, and by oxidation it is changed to **β-naphtho-quinone-carboxylic acid** (B. **28,** 3089). From sodium α-naphtho-hydroquinone and CO_2 we obtain **1, 4-dioxy-2-naphthoic acid,** m.p. 186° with decomposition, and also a condensation product of the anthracene series (*J. pr. Ch.* 2, **62,** 47). **1, 3-Dioxy-2-naphthoic acid,** *naphtho-resorcin-carboxylic acid,* m.p. 145° with decomposition, has been obtained by saponifying its ethyl ester, m.p. 83°, formed synthetically by the action of concentrated H_2SO_4 upon phenyl-acetyl-malonic ester (A. **298,** 383). For other dioxy-naphthoic acids, see B. **29,** 39.

D. *Naphthalene-di- and poly-carboxylic Acids.*—Six of these acids

are known. It is remarkable that the 1, 8- or peri-acid, so-called **naphthalic acid** $C_{10}H_6[1, 8](COOH)_2$, is produced by the oxidation of acenaphthene and also from its *semi-nitrile*, which is made by saponifying the diazo-derivative of peri-amido-naphthoic acid. The following diagram represents the relations of a series of *peri-naphthalene derivatives* :



Just as in the case of other peri-derivatives, so here naphthalic acid when heated to 180° breaks down without melting into water and its *anhydride* $C_{10}H_6(CO)_2O$, melting at 266°, which also forms easily on treating the acid with alcoholic HCl, and in many other processes. Like phthalic anhydride, it condenses with phenol to *phenol-naphthalein* $C_{10}H_6\langle^{C(C_6H_4OH)_2}_{CO\cdot\cdot>O}$ (B. **28,** R. 621); with malonic acid ester and $ZnCl_2$ to peri-naphtho-indandione $C_{10}H_6\{^{[1]CO}_{[8]CO}CH_2$ (C. 1911, I. 1633). Naphthal-imide $C_{10}H_6(CO)_2NH$, m.p. 300°, when treated with sodium hypochlorite gives naphtho-styrile (B. **43** 440). Cp. B. **28,** 360; **32,** 3283; C. 1902, II. 898; A. **327,** 77 for naphthal-imide, -anile, and -phenyl-hydrazile. **1, 2-Naphthalene-dicarboxylic acid,** obtained by the saponification of its nitrile, melts at 175° and passes into its *anhydride*, melting at 105° (B. **25,** 2475). **1, 5-Naphthalene-dicarboxylic acid,** B. **29,** R. 516.

1-Phenyl-naphthalene-2, 3-dicarboxylic acid $C_6H_4\langle^{CH=\!=\!=CCOOH}_{C(C_6H_5):CCOOH}$ is formed as an anhydride, m.p. 255°, in a reaction recalling the formation of benzene rings from acetylenes, on heating phenyl-propiolic acid $C_6H_5C:CCOOH$ with acetic anhydride and on illuminating a benzene solution of dibenzal-succinic anhydride. By the action of concentrated H_2SO_4 the colourless anhydride passes into **allo-chryso-keto-carboxylic acid,** m.p. 288°, in claret-coloured needles, which, on fusing with alkali, yields an isomeric **1-phenyl-naphthalene-dicarboxylic acid,** m.p. 288° (B. **40,** 3372, 3839; C. 1908, II. 1357):

$$C_{10}H_5\{^{C_6H_5}_{CO}\rangle O \longrightarrow C_{10}H_5\langle^{COOH}_{C_6H_4}\rangle CO \longrightarrow C_{10}H_6COOH\cdot C_6H_4COOH$$

Naphthalene-tetracarboxylic acid $C_{10}H_4[1, 4, 5, 8](CO_2H)_4$, with the

carboxyl groups in the two peri-positions of naphthalene, results when pyrenic acid is oxidised (B. **20**, 365).

Naphtho-nitriles, Cyano-naphthalenes.—Naphtho-nitriles may be obtained by the distillation of the alkali salts of the naphthalene-disulphonic acids, or the phosphoric esters of the naphthols with potassium cyanide or yellow prussiate of potash (B. **21**, E. 834), or from the naphthylamines by means of the diazo-compounds.

α-Naphtho-nitrile, α-cyano-naphthalene $C_{10}H_7.CN$, melting at 37° and boiling at 298°, has also been prepared from formo-naphthalide $C_{10}H_7.NH.COH$.

β-Cyano-naphthalene melts at 66° and boils at 304°. **1, 2-Dicyano-naphthalene** $C_{10}H_6[1, 2](CN)_2$, melting at 190°, is produced when 1, 2-chloro-naphthalene-sulphonic acid is distilled with potassium ferro-cyanide (B. **25**, 2475). For additional isomeric dicyano-naphthalenes, see A. **152**, 289; J. 1869, 483, etc.

1, 4-Dicyano-2, 3-dioxy-naphthalene $C_6H_4 \begin{cases} C(CN) : COH \\ C(CN) : COH \end{cases}$, m.p. 291°, is formed by nuclear synthesis in the condensation of oxalic ester with o-xylylene cyanide.

12. **Dinaphthyl-, Dinaphthyl-methane,** and **Trinaphthyl-methane Derivatives.**—Different isomeric **dinaphthyls** have been made by conducting the vapours of naphthylene through bronze tubes heated to redness, by heating naphthalene with Al_2Cl_6, or from bromo-naphthalene and iodo-naphthalene with sodium, and by heating mercury dinaphthyl $Hg(C_{10}H_7)_2$, etc. (B. **28**, R. 184).

The αα-dinaphthyl, on heating with $AlCl_3$ to 140°, joins the two naphthalene residues in the peri-position and yields a hydrocarbon consisting of five condensed benzene-rings, and called **perylene** $C_{10}H_6 \begin{cases} [1] \\ [8] \end{cases} C_{10}H_6$, bronze-coloured flakes, b.p. 262°–265°, the constitution of which is determined by its formation from 1, 8-di-iodo-naphthalene on heating with copper bronze (B. **43**, 2202). The 4, 4-diamido-1, 1-dinaphthyl or naphthidins, corresponding to the benzidins or **4, 4-diamido-diphenylenes,** are formed besides the **1, 1-diamido-2, 2-dinaphthylene** or **dinaphthylinene,** by transformation of hydrazo-naphthalenes, or direct from the naphthylamines by the action of 80 per cent. sulphuric acid, in the presence of oxidising agents such as ferric oxide (B. **25**, R. 949). In the same way the naphthols give **dinaphthols** with ferric chloride. On binuclear quinones of the dinaphthyl series, see *J. pr. Ch.* 2, **62**, 31; B. **42**, 1058.

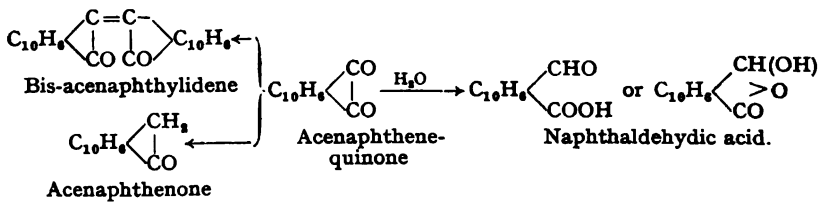
Dinaphthyl-methanes and their derivatives are formed by methods used in forming the diphenyl-methane series: **α_2- and β_2-dinaphthyl-methane** $CH_2(C_{10}H_7)_2$, m.p. 109° and 92°; **α, β-dinaphthyl-methane,** m.p. 96°, see B. **44**, 449; **α_3-trinaphthyl-methane** $(C_{10}H_7)_3CH$, m.p. 101°, from its carbinol by reduction with HI in glacial acetic acid (B. **44**, 1105). **Trichloro-ethylidene-αα-dinaphthyl** $CCl_3CH(C_{10}H_7)_2$, m.p. 156°, on heating with alcohol and zinc dust, is converted into **αα-naphtho-stilbene** $C_{10}H_7CH : CHC_{10}H_7$, m.p. 161°. The latter is closely related to picene, into which it is converted on superheating. **ββ-Naphtho-stilbene,** m.p. 255° (B. **38**, 509). From naphthylamine, and from naphtholene with aldehydes, we obtain, with particular ease, alkylidene-dinaphthyl-

amines (C. 1900, II. 481) and alkylidene-dinaphthols. The products formed from β-naphthol with aldehydes part with water and become *xanthenes*, hence they in all probability contain the alkylidene groups in the o-position with reference to the hydroxyls: **β-dinaphthol-methane**, melting at 190°, yields, with $POCl_3$, *dinaphtho-xanthene* $C_{10}H_6\langle{}^{O}_{CH_2}\rangle C_{10}H_6$, while benzaldehyde and β-naphthol at once form ms-*phenyl-naphtho-xanthene* $C_6H_5CH(C_{10}H_6)O$ (B. **25**, 3477; **26**, 83), together with an acetal. Sodium-β-naphthol and chloroform at 150° produce an anhydride of *trioxy-trinaphthyl-methane* $HOC_{10}H_6CH[C_{10}H_6]_2O$, m.p. 273°, which is also formed by the condensation of β-naphthol and β-naphthol-aldehyde (C. 1901, I. 945, 1010).

αα- and ββ-**Dinaphthyl-carbinol** $(C_{10}H_7)_2CHOH$, from α- and β-naphthyl-magnesium bromide and formic ester; *aaa*- and **aaβ-trinaphthyl-carbinol** $(C_{10}H_7)_3COH$, m.p. 169° and 264°. The dinaphthyl-carbinols, but, strangely enough, not the trinaphthyl-carbinols, show the same mobility of the hydroxyl group as the diphenyl- and triphenyl-carbinol. HCl easily produces the corresponding chlorides $(C_{10}H_7)_2CHCl$, from which αα- and **ββ-dinaphthyl-acetic acid** $(C_{10}H_7)_2CHCOOH$, m.p. 228° and 179° respectively, are obtained, with Mg and CO_2. On treatment with zinc and HCl, the dinaphthyl-carbinols easily split off water and pass into αα- and *ββ-dinaphtho-fluorene* (B. **42**, 2377; **43**, 2824).

Numerous dyes of the naphthyl-diphenyl, dinaphthyl-phenyl, and trinaphthyl series have been prepared by known methods, but are of no practical interest, on account of their slight solubility and high price (B. **37**, 1899).

13. **Acenaphthene.**—Acenaphthene, or *peri-ethylene-naphthylene* $C_{10}H_6\langle{}^{[1]CH_2}_{[8]CH_2}$, melting at 95° and boiling at 277°, is a peculiar derivative of naphthalene, which is obtained by conducting α-ethyl-naphthalene through a red-hot tube, or by the action of alcoholic potash upon *α-bromo-ethyl-naphthalene* $C_{10}H_7.C_2H_4Br$. It also occurs in coal-tar. Inasmuch as acenaphthene is oxidised by sodium bichromate and sulphuric acid to naphthalic acid, the side chain C_2H_4 must be arranged in the two peri-positions (1 and 8) of naphthalene. **Acenaphthene-quinone** $C_{10}H_6(CO)_2$, melting at 261°, is a by-product in this oxidation. Zinc dust and acetic acid reduce it to **acenaphthenone** $\overline{C_{10}H_6.CH_2.CO}$, melting at 121°, while hydriodic acid and phosphorus change it to **bis-acenaphthylidene** $(\overline{C_{10}H_6.CO.C}:)_2$, melting at 294°, and alkalies decompose it into *naphthaldehydic acid* (B. **26**, R. 710; A. **290**, 195; C. 1899, II. 378; 1909, II. 775):



The monoxime of acenaphthene-quinone $C_{12}H_6O(NOH)$, m.p. 230°,

is converted into naphthalimide by Beckmann's transposition (C. 1903, I. 881).

By bromination, nitration, or acidulation, acenaphthene is substituted in the 4-position, as shown by the conversion of the corresponding derivatives into derivatives of naphthalic acid (A. **327**, 77; **B. 43**, 2473).

Acenaphthene-quinone easily unites in the presence of condensing agents like $AlCl_3$, $ZnCl_2$, with aromatic hydrocarbons, amines, and phenols to form diaryl-acenaphthenones $C_{10}H_6\langle^{CO}_{C(R)_2}$ (B. **43**, 2915).

9, 9-Diphenyl-acenaphthenone $C_{10}H_6\langle^{CO}_{C(C_6H_5)_2}$, m.p. 174°, results also from the 9, 10-diphenyl-acenaphthene-glycol $C_{10}H_6\langle^{C(OH)C_6H_5}_{C(OH)C_6H_5}$, m.p. 156°, the product of the action of C_6H_5MgBr upon acenaphthene-quinone on heating with concentrated HCl (pinacolin transposition).

With indoxyl and thio-indoxyl (β-oxy-thio-naphthene) acenaphthene-quinone condenses to a violet or red vat dye $C_6H_4\langle^{CO}_{NH}\rangle C:C\langle^{CO}_{C_{10}H_6}$ and $C_6H_4\langle^{CO}_{S}\rangle C:C\langle^{CO}_{C_{10}H_6}$ (B. **41**, 3331; C. 1909, II. 775).

When the vapour of acenaphthene is conducted over lead oxide heated to redness, two atoms of hydrogen split off and **acenaphthylene** $C_{10}H_6\langle^{CH}_{CH}\|$ results. This forms *yellow* plates (B. **26**, 2354), melts at 92°, and boils at 270° with decomposition. Chromic acid also oxidises it to naphthalic acid.

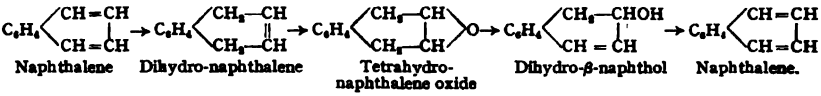
On a synthesis of substituted acenaphthylenes, see A. **369**, 157. On heating acenaphthene with sulphur to about 290°, we obtain **dinaphthylene-thiophene** $C_{10}H_6\{^{C\text{——}C}_{C\text{—}S\text{—}C}\}C_{10}H_6$, red needles, m.p. 278°, beside the yellow hydrocarbon $[C_{10}H_6\langle^{C}_{C}]_3$: **trinaphthylene-benzol**, m.p. 387° (B. **36**, 962). By reduction with hydrogen and finely divided nickel we obtain from acenaphthene **tetrahydro-acenaphthene**, b.p. 254° (C. 1901, II. 202) and **decahydro-acenaphthene**, b.p. 230°–234° (B. **42**, 2094).

14. Hydro-naphthalene Derivatives.

Hydro-naphthalene compounds attach themselves to naphthalene just as the hydro-aromatic benzene derivatives do to benzene. Naphthalene and its derivatives take up hydrogen and the halogens more readily than the compounds of benzene. Those naphthalene derivatives which have added hydrogen to *one* nucleus alone are remarkable and interesting, because they manifest in one substance the differences which prevail between an *aromatic* and a *hydro-aromatic* or *alicyclic* nucleus. While the non-hydrogenised nucleus of the respective naphthalene compounds retains the aromatic properties, the hydrogenised *alicyclic* nucleus assumes, on the contrary, the nature of a fatty radicle, and as a consequence the whole system acquires the character of an homologous benzene derivative (Bamberger, A. **257**, 1).

A. **Dihydro-naphthalene Derivatives.—Dihydro-naphthalene** $C_{10}H_{10}$, melting at 15° and boiling at 212°, is formed when naphthalene is

reduced with sodium in a boiling ethyl-alcohol solution. The entering hydrogen atoms assume the 1, 4-position, because the hydride yields o-phenylene diacetic acid when it is oxidised. It can be viewed as the hydrocarbon of α-naphtho-quinone. Dihydro-naphthalene resembles the olefins—*e.g.* ethylene—in that it readily takes up two univalent atoms or radicles. Thus with bromine it forms a ***dibromide***, with hypochlorous acid a ***glycol-chloro-hydrin***. ***Tetrahydro-naphthylene oxide*** can be easily obtained from the latter, and is capable of rearranging itself to **1, 2-dihydro-β-naphthol** $C_{10}H_{10}O$, boiling at 162°–168° (28 mm.), which may be oxidised to dihydro-iso-cumarin-carboxylic acid, and when it splits off water naphthalene is produced (A. **288,** 74) :



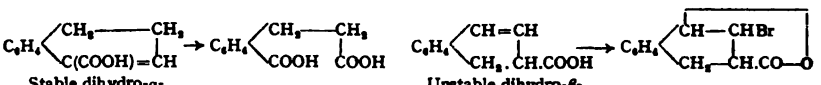
Phenyl-hydro-naphthalene $C_6H_4\langle^{CH(C_6H_5).CH}_{CH_2\text{———}CH}$, m.p. 50°, results from phenyl-bromo-tetrahydro-naphthoic acid on boiling with soda solution, or, better, with diethyl-aniline (A. **306,** 235).

Naphthalene dichloride $C_{10}H_8Cl_2$ is a yellow oil formed when naphthalene is treated with potassium chlorate and hydrochloric acid. It changes to α-chloro-naphthalene at 40°–50°, and by the elimination of hydrogen chloride.

Dihydro-naphthoic Acids.—Sodium amalgam reduces the α- and β-naphthoic acids, two hydrogen atoms being added to the nucleus already carrying the carboxyl group, and in the cold there result ***unstable***, and when heat is applied ***stable***, **dihydro-naphthoic acids** $C_{10}H_9.CO_2H$. The former are unsaturated at β and γ, the latter at α and β :

α-Stable melting at 125° ; β-stable melting at 161°.
α-Unstable ,, 91° ; β-unstable ,, 104°.

The unstable modifications pass into the stable modifications on boiling them with caustic soda. Potassium permanganate oxidises the stable α-acid to hydro-cinnamic acid, while the unstable acid yields oxalic acid and phthalic acid. The dibromide of the unstable β-acid, in contrast with the stable modification, readily changes to a brominated lactone. All these facts point to the following formulæ for the stable α- and the unstable β-acid (A. **266,** 169) :



The dihydro-β-acids, when oxidised with potassium ferricyanide, revert again to β-naphthoic acid.

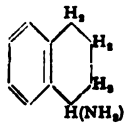
The stable α-dihydro-naphthoic acid, like other α, β-unsaturated carboxylic acids, adds sodium-aceto-acetic ester with formation of a δ-ketonic acid ester, which, however, immediately discards alcohol, and condenses to a phenanthrene (B. **31,** 1896).

α-Phenyl-dihydro-β-naphthoic acid $C_{10}H_8(C_6H_5)COOH$, m.p. 191°,

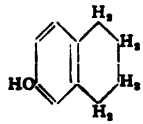
is obtained by condensation of dibenzyl-propionic acid by means of glacial acetic sulphuric acid (A. **306**, 156).

B. **Tetrahydro-naphthalene Derivatives.**—**Tetrahydro-naphthalene** $C_{10}H_{12}$, boiling at 206°, is formed in the reduction of naphthalene with sodium in amyl alcohol solution; also from ar-tetrahydro-naphthylamine by the elimination of the NH_2 group; hence the H atoms are only present in the one nucleus. **Naphthalene tetrachloride** $C_{10}H_8Cl_4$, melting at 182°, is produced when chlorine is conducted into a chloroform solution of naphthalene. Boiling alcoholic potash changes it to dichloro-naphthalene. See B. **28**, R. 392, for the oxidation of naphthalene tetrachloride. Consult B. **24**, R. 713, for the chlorine addition products of chlorinated and sulphur-containing naphthalenes. **Naphthalene tetrabromide** melts at 111° (C. 1897, I. 984).

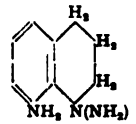
The naphthylamine and naphthol hydrides are particularly interesting. Sodium acting upon the boiling amyl alcohol solution of the naphthols and naphthylamines causes these bodies to add four hydrogen atoms each to one nucleus. If the latter carries the NH_2 or OH group, the body formed no longer possesses the character of a naphthylamine or a naphthol, but has that of a benzene homologue, amidated or bearing the OH group in the side chain. Should, however, the non-substituted nucleus be hydrogenised, then the products acquire the nature of homologous anilines or phenols. E. Bamberger, who first observed these relations and explained them, designated the second class of tetrahydro-derivatives as *aromatic* (ar-), and the first class as *aliphatic-cyclic* or *alicyclic* (ac-):



ac-Tetrahydro-α-naphthylamine



ar-Tetrahydro-β-naphthol



ar-, ac-Tetrahydro-1, 5-naphthylene-diamine.

α-Naphthylamine and α-naphthol upon reduction yield ar-tetrahydro-α-naphthylamine and naphthol, while the β-compounds form both the ar- and the ac-tetrahydro-derivative; the latter predominates. 1, 5-Naphthylene-diamine yields ac-, ar-tetrahydro-naphthylene-diamine, which, by elimination of the aromatic NH_2 group, forms ac-tetrahydro-α-naphthylamine.

ar-Tetrahydro-naphthylamines $NH_2.C_6H_3 : (C_4H_8)$. The α-body boils at 275° and the β-form at 276°. They are feeble bases and form diazo- and azo-compounds. They exercise a reducing power with salts of the noble metals. By oxidation with potassium permanganate all yield adipic acid and oxalic acid.

Chromic acid oxidises the α-compound to **ar-tetrahydro-α-naphtho-quinone** $C_6H_2O_2 : (C_4H_8)$, melting at 55°, which in every respect resembles benzo-quinone and possesses much greater oxidising power than α-naphtho-quinone. **ac-Tetrahydro-naphthylamines** $C_6H_4 : (C_4H_7.NH_2)$; the α-body boils at 246° and the β- at 249°. They are strong bases, which absorb carbon dioxide from the air. They do not form diazo-derivatives. Potassium permanganate ruptures the hydro genised ring and produces o-cinnamo-carboxylic acid.

From the β-, ac-tetrahydro-naphthylamine, by means of d-bromo-

camphoro-sulphonic acid, an optically active dextro-rotatory modification has been obtained (C. 1899, II. 255 ; 1900, I. 862).

ac-, ar-Tetrahydro-1, 5-naphthylene-diamine $NH_2.C_6H_3:(C_4H_7NH_2)$, melting at 77° and boiling at 261°, combines in itself both the properties of an aromatic and of an alicyclic amine. It contains an asymmetric carbon atom, and has been resolved into a dextro- and a lævo-modification.

ar-Tetrahydro-α-naphthol $OH.C_6H_3:(C_4H_8)$, melting at 69° and boiling at 265°, is also derived from ar-tetrahydro-α-naphthylamine by means of the diazo-derivative.

ac-Tetrahydro-β-naphthol $C_6H_4:(C_4H_4OH)$ is an oil, boiling at 264°. It exhibits the character of a fatty alcohol and resembles similarly constituted camphor alcohols, like menthol and borneol.

A series of tetrahydro-naphthalene derivatives has been obtained, starting with dihydro-naphthalene : Thus, phenol and the latter form **tetrahydro-naphthyl-phenol** $C_6H_4:(C_4H_7.C_6H_4OH)$, boiling at 130° (B. **24,** 179), while bromine changes it to **dihydro-naphthalene dibromide** $C_6H_4:(C_4H_6Br_2)$. Boiling potassium carbonate, or transformation with silver acetate and subsequent saponification, converts the latter into **tetrahydro-naphthylene glycol** $C_6H_4\langle^{CH_2—CHOH}_{CH_2—CHOH}$, melting at 135° (cis-form) and 118° (trans-form), which by oxidation is broken down into o-phenylene-diacetic acid. It is an analogue of ethylene-glycol. The *chloro-hydrin* (above) $C_{10}H_{10}Cl(OH)$, melting at 117°, with caustic potash yields **tetrahydro-naphthylene oxide** $C_{10}H_{10}O$, melting at 43° and boiling at 258°, which manifests all the chemical properties of ethylene oxide (I. 298). Bases have converted the chloro-hydrin into a series of "*alkines*," of which mention may be made of—

Trimethyl - oxy - tetrahydro - naphthylene - ammonium hydroxide $C_6H_4\langle^{CH_2.CHOH}_{CH_2.CHN(CH_3)_3OH}$, because of its intimate connection with choline (I. 309). The feebler alkalies convert this oxide into the isomeric **β-keto-tetrahydro-naphthalene** $C_6H_4\langle^{CH_2—CH_2}_{CH_2—CO}$, melting at 18° and boiling at 138° (16 mm.), which can also be prepared by the distillation of o-phenylene-propion-acetic acid (B. **28,** 745). It behaves like a fatty ketone (B. **27,** 1547) with sodium bisulphite, phenyl-hydrazin, and hydroxylamine. **α-Keto-tetrahydro-naphthalene** $C_6H_4\langle^{CH_2—CH_2}_{CO—CH_2}$ is obtained by intramolecular condensation of γ-phenyl-butyric acid chloride by means of $AlCl_3$ (C. 1899, I. 792).

The chlorine addition products of the naphtho-quinones are *diketo-tetrahydro-naphthalene derivatives.* They result from the action of Cl upon the corresponding dioxy-naphthalenes or naphtho-quinones (A. **300,** 180 ; **334,** 342) :

$$C_6H_4\langle^{CO—CO}_{CCl_2—CCl_2}, \quad C_6H_4\langle^{CO—CCl_2}_{CO—CCl_2}, \quad C_6H_4\langle^{CO—CCl_2}_{CCl_2—CO}, \quad C_6H_4\langle^{CCl_2—CO}_{CCl_2—CO}.$$

Diketo-tetrahydro-naphthylene oxide $C_6H_4\langle^{CO—CH}_{CO—CH}\rangle O$, melting at 136°, is produced by the action of bleaching-lime upon α-naphtho-quinone (p. 671 and A. **286,** 71).

The *tetrahydro-naphthoic acids* are also classified into aromatic and alicyclic. **ar-Tetrahydro-α-naphthoic acid** $COOH.C_6H_3:(C_4H_8)$, with an *amide* melting at 182°, is derived from its nitrile, a rearrangement product from ar-tetrahydro-α-naphthalene-diazo-chloride and potassio-copper cyanide.

ac-Tetrahydro-naphthoic acids, the α- melting at 85° and the β- at 96°, are formed when naphthoic and dihydro-naphthoic acids are reduced with sodium amalgam. They resist the action of potassium permanganate more strongly than the dihydro-acids. In comparison with the latter they thus prove themselves to be saturated acids. The long-continued action of the oxidant finally changes them to phthalic and oxalic acids (A. **266,** 202).

For the splitting up of the tetrahydro-naphthoic acids into their optically active components, see C. 1906, II. 962.

ac-Phenyl-tetrahydro-β-naphthoic acid $C_6H_4[C_4H_6(C_6H_5)COOH]$, m.p. 177°, results from the reduction of phenyl-bromo-tetrahydro-naphthoic acid, m.p. 205°, obtained synthetically by the action of Br at 0° upon the chloroform solution of benzyl-phenyl-iso-crotonic acid (A. **306,** 231).

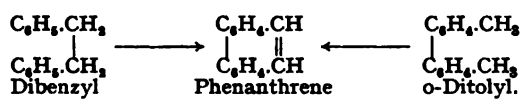
ac-Tetrahydro-naphthalene-dicarboxylic acid $C_6H_4[C_4H_6(CO_2H)_2]$, melts at 199°, with the production of its anhydride, melting at 184°. The latter is also formed on heating potassium tetrahydro-naphthalene tetracarboxylate, the ester of which has been synthesised from o-xylylene bromide and the sodium derivative of the dimalonic acid ester (B. **17,** 448). **Tetrahydro-1, 5-naphthalene-dicarboxylic acid** melts at 238° (B. **29,** R. 517).

C. **Hexa-, octo-, deca-, and dodecahydro-naphthalenes** $C_{10}H_{14}$, $C_{10}H_{16}$, $C_{10}H_{18}$, and $C_{10}H_{20}$, boil at 200°, 185°–190°, 173°–180°, and 153°–158° respectively. They have been obtained by the action of hydriodic acid and phosphorus upon naphthalene (B. **16,** 796, 3032; A. **187,** 164).

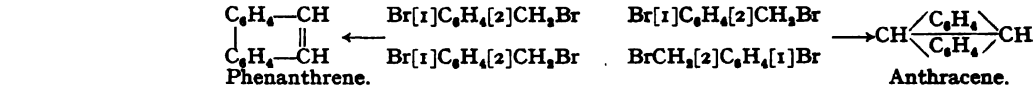
Decahydro-naphthalene has also been obtained by reduction with H and Ni at 160°. **Deca-hydro-α- and -β-naphthol** $C_{10}H_{17}OH$, m.p. 62° and 75°, b.p.$_{14}$ 109° and 112°, are easily formed by the reduction of α- and β-naphthol with H and Ni; by rejection of water they yield two isomeric **octohydro-naphthalenes,** b.p. 190° and 191°, by oxidation with CrO_3 the corresponding ketones $C_{10}H_{16}O$, m.p. 32° and b.p. 240°, the oximes of which are reduced by Na and alcohol to α- and **β-deca-hydro-naphthylamine** $C_{10}H_{17}NH_2$, b.p.$_{14}$ 97° and 112° (C. 1911, I. 318).

III. Phenanthrene Group.

Phenanthrene occurs, together with anthracene, in coal-tar and in the so-called "stubb," a substance obtained (together with fluoranthene and pyrene) in the distillation of mercury ores in Idria. It is prepared synthetically (1) (with diphenyl, anthracene, and other hydrocarbons) from various benzene compounds, by conducting their vapours through a red-hot tube—*e.g.* from toluene, stilbene, diphenyl, and ethylene, and particularly from dibenzyl and o-ditolyl:

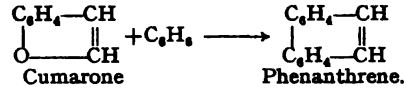


(2) Sodium acting on o-bromo-benzyl bromide also produces it, together with anthracene.



Phenanthrene. Anthracene.

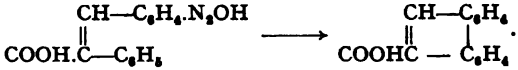
(3) It also appears in the condensation of cumarone with benzene (B. **23,** 85) :



Cumarone Phenanthrene.

Chrysene is similarly formed from cumarone and naphthalene, and amido-naphthalene (p. 694) from furfurane and aniline.

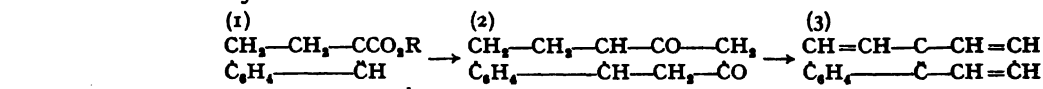
(4) When the diazo-derivative of o-amido-α-phenyl-acetic acid is acted upon with copper powder, phenanthrene-carboxylic acids (B. **29,** 496) result :



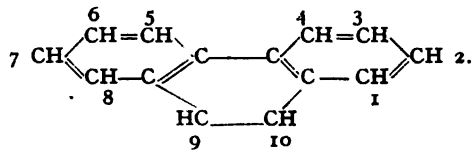
This reaction recalls the formation of diphenyl from benzene and diazo-benzene, as well as that of diphenyl-ketone from the diazo-derivative of o-amido-benzo-phenone.

(5) Quite analogous to the synthesis of α-naphthol from phenyl-iso-crotonic acid is the formation of 4-oxy-phenanthrene by heating **β-naphthyl-iso-crotonic acid** $C_{10}H_7\langle^{[\beta]CH=CH}_{HOCO-CH_2}$ ⟶ $C_{10}H_6\langle^{CH=CH}_{C(OH):CH}$

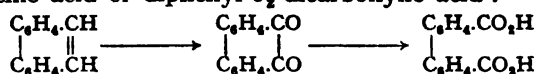
(6) The following synthesis of phenanthrene, starting from a naphthalene derivative, is of interest : Dihydro-β-naphthoic acid ester (1) condenses with aceto-acetic ester to a diketo-octohydro-phenanthrene-carboxylic ester, which, on saponification and rejection of CO_2, yields octohydro-diketo-phenanthrene (2), which in turn gives phenanthrene by zinc-dust distillation.



Phenanthrene in accordance with these methods of production must be viewed as a derivative of diphenyl, in which two ortho-positions of the two benzene rings are joined by the group CH=CH, which therefore constitutes, with the four carbon atoms of the two benzene rings, a third normal benzene ring :



The oxidation of phenanthrene leads to a similar conclusion. Phenanthraquinone is the first product, and by continued oxidation it yields diphenic acid or diphenyl-o_2-dicarboxylic acid :



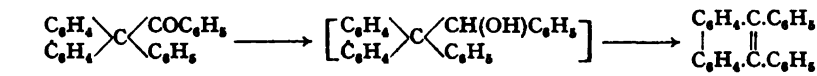
Phenanthrene Phenanthraquinone Diphenic acid.

Since phenanthrene and its derivatives have been obtained as disintegration products of the important alkaloids **morphia, codeïn,** and **thebain,** the chemistry of the phenanthrenes has, of late, been carefully studied.

Phenanthrene $C_{14}H_{10}$ crystallises in colourless plates, melting at 99° and boiling at 340°. It dissolves readily in ether and benzene, but with more difficulty in alcohol and water. The solutions exhibit a blue fluorescence.

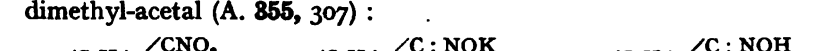
The picrate $C_{14}H_{10}.C_6H_2(NO_2)_3.OH$ separates in yellow needles, melting at 144°. Consult A. **196,** 34; B. **19,** 761, for a method of isolating phenanthrene from crude anthracene.

Alkylated Phenanthrenes.—**1-** and **3-methyl-phenanthrene** $C_{14}H_9.CH_3$, m.p. 123° and 65°, result from the synthetic 1- and 3-methyl-phenanthrene-9-carboxylic acids by rejection of CO_2. **9, 10-Dimethyl-phenanthrene** $C_{14}H_8(CH_3)_2$, m.p. 139°, by reduction of 9, 10-dimethyl-9, 10-dioxy-dihydro-phenanthrene with HI and phosphorus (B. **39,** 3110; A. **362,** 250). **9, 10-Diphenyl-phenanthrene** $C_{14}H_8(C_6H_5)_2$, m.p. 235°, has been obtained by nuclear synthesis by the action of $AlCl_3$ upon tetraphenyl-ethylene (B. **38,** 203). It is also produced by a remarkable atomic displacement in the reduction of benzoyl-phenyl-fluorene with HI and phosphorus, a reaction corresponding to the formation of tetraphenyl-ethylene from β-benzo-pinacolin (B. **37,** 2887):



Halogen Phenanthrenes.—By the action of chlorine upon phenanthrene substitution products are formed: **9, 10-dichloro-** and **2, 9, 10-trichloro-phenanthrene** $C_{14}H_8Cl_2$ and $C_{14}H_7Cl_3$, m.p. 161° and 124° (B. **39,** 3891); **octochloro-phenanthrene** $C_{14}H_2Cl_8$, m.p. 270°–280°, is split up on further chlorination into C_6Cl_6 and CCl_4. Bromine in CS_2 solution forms an addition product, phenanthrene dibromide $C_{14}H_{10}Br_2$, which splits off HBr and passes into **9-bromo-phenanthrene** $C_{14}H_9Br$, m.p. 63°. The latter is oxidised by chromic acid to phenanthrene-quinone, and on further bromination to **4, 9-(4, 10-) dibromo-phenanthrene** $C_{14}H_8Br_2$, m.p. 112°–113°, which on oxidation yields 4-bromo-phenanthrene-quinone (A. **321,** 330; B. **37,** 3553).

Nitro-phenanthrenes.—The nitration of phenanthrenes produces three nitro-phenanthrenes, one of which has been found to be **3-nitro-phenanthrene** $C_{14}H_9[3]NO_2$, m.p. 170°–171° (B. **34,** 3532). If a mixture of acetic anhydride and nitric acid is nitrified in glacial acetic acid we obtain **9-nitro-phenanthrene,** m.p. 116°–117°, which is also obtained from the product of the action of gaseous nitrous acid upon phenanthrene by treatment with sodium ethylate solution (B. **36,** 2508). By boiling with methyl-alcoholic potash the 9-nitro-phenanthrene takes up two molecules CH_3OK and transposes into the isomeric phenanthrene-quinone-monoxime by way of phenanthrene-quinone-oxime-dimethyl-acetal (A. **355,** 307):



Compare the similar transposition of 7-nitro-stilbene, of 1- and 2-nitro-naphthalene, and of 9-nitro-anthracene.

Amido-phenanthrenes, **phenanthrylamines,** have been obtained partly by the reduction of the nitro-phenanthrenes, partly from the phenanthrols by heating with ammonia salts : **2-amido-phenanthrene** $C_{14}H_9(NH_2)$, m.p. 85°, **3-amido-phenanthrene**, m.p. 87° ; **9-amido-phenanthrene,** m.p. 135°–136°, have also been obtained from the azide of 9-phenanthrene-carboxylic acid (A. **321,** 312 ; B. **34,** 1461 ; **35,** 2726). **9, 10-Diamido-phenanthrene** $\begin{matrix}C_6H_4—CNH_2\\C_6H_4—CNH_2\end{matrix}$, from phenanthrene-quinone-dioxime by reduction, gives by atmospheric oxidation **diphenanthryl-azin** $C_{14}H_8 : N_2 : C_{14}H_8$ (B. **35,** 2738).

Phenanthrene-sulphonic Acids.—On sulphurising phenanthrene we obtain **3-, 2-,** and **9-phenanthrene-sulphonic acids,** $C_{14}H_9.SO_3H$ (3-sulpho-chloride, m.p. 108°, 2-sulpho-chloride, m.p. 156°, 9-sulpho-chloride, m.p. 125°), whose constitution has been determined by converting them into oxy- and cyano-phenanthrenes (A. **321,** 251 ; **369,** 104 ; **379,** 79 ; B. **34,** 4004).

Oxy-phenanthrenes, phenanthrols, have been obtained by fusion with potash from the sulphonic acids and from the phenanthryl-amines, while their ethers have also been obtained by the synthetic methylated phenanthrene-9-carboxylic acids by rejection of CO_2, which has fixed the constitution of the five possible and known isomerides : **1-methoxy-phenanthrene** $C_{14}H_9$-[1-](OCH$_3$), m.p. 106°, **2-phenanthrol** $C_{14}H_9$[2]OH, m.p. 168° (methyl ether, m.p. 99°), **3-phenanthrol,** m.p. 124° (methyl ether, m.p. 63°), **4-phenanthrol,** m.p. 108° (methyl ether, m.p. 68°), formed by nuclear synthesis on heating β-naphthyl iso-crotonic acid.

9-Phenanthrol, *phenanthrone* $\begin{matrix}C_6H_4—CH\\C_6H_4—COH\end{matrix}$ or $\begin{matrix}C_6H_4—CH_2\\C_6H_4—CO\end{matrix}$, m.p. 153°, is also formed by the reduction of phenanthraquinone with HI, or from phenanthrene-quinone dichloride $C_{14}H_8OCl_2$; it gives, with diazo-benzol salts, the **10-benzol-azo-9-phenanthrol,** m.p. 165°, which is identical with the product of the action of phenyl-hydrazin upon phenanthraquinone ; 2-, 3-, and 9-phenanthrol resemble β-naphthol (A. **321,** 276 ; B. **34,** 1461, 3998 ; **41,** 4215). Of the amido-phenanthrols (A. **321,** 286, 295) and the dioxy-phenanthrenes, the 9, 10-derivatives should be separately mentioned. **9, 10-Amido-oxy-phenanthrene** $C_{12}H_8\begin{matrix}C(OH)\\C(NH_2)\end{matrix}$ from phenanthrene-quinone-oxime, -imine or phenyl-hydrazone, by reduction easily passes into **phenanthrene-hydroquinone,** 9, 10-*dioxy-phenanthrene* $C_{14}H_8(OH)_2$, m.p. 147°–148°, which is best formed by reduction with zinc and glacial acetic acid, or with H_2S in alcoholic solution. Nitro-phenanthrene-hydroquinones have been obtained similarly (B. **35,** 3117).

3, 4-Dimethoxy-phenanthrene, *dimethyl-morphol* $C_{14}H_8(OCH_3)_2$, m.p. 44°, from 9-carboxylic acid, or by methylating the corresponding monomethyl-ether, **methyl-morphol** $C_{14}H_8(OH)(OCH_3)$, which is a product of the decomposition of the alkaloid codeïn (*q.v.*) (B. **33,** 1816). **3, 4, 5-Trioxy-phenanthrene** $C_{14}H_7(OH)_3$, m.p. 148°, is formed by fusing morphinol with caustic potash (B. **39,** 1718).

Phenanthrene-carboxylic Acids.—Their nitriles have been obtained from the salts of the sulphonic acids by distillation with potassium ferrocyanide. 9-Phenanthrene-carboxylic acid and its substitution pro-

ducts have also been obtained synthetically by method 4 (above). **2-, 3-,** and **9-Cyano-phenanthrene** $C_{14}H_9.CN$, m.p. 105°, 102°, and 103°; **2-, 3-,** and **9-phenanthrene-carboxylic acids,** m.p. 254°, 269°, and 250° (A. **321,** 322). **8, 9-Phenanthrene-dicarboxylic acid,** anhydride, m.p. 284°, synthetically by method 4 (B. **39,** 3115).

1-, 2-, 3-, and **4-Methoxy-phenanthrene-9-carboxylic acid** $C_{14}H_8(OCH_3)CO_2H$, m.p. 215°, 228°, 239°, and 224°, and 3, 4-dimethoxy-phenanthrene-9-carboxylic acid $C_{14}H_7(OCH_3)_2COOH$, m.p. 228°, from the corresponding methoxy-amido-α-phenyl-cinnamic acids, split off CO_2 on distillation and form methoxy-phenanthrenes (B. **34,** 3998). **2, 3-** and **3, 2-Phenanthrol-carboxylic acid** $C_{14}H_8(OH).CO_2H$, m.p. 227° with decomposition and 303° with decomposition, have been obtained by a salicylic acid synthesis by 2- and 3-sodium-phenanthrol by heating with CO_2 under pressure. They are coloured yellow and resemble 2, 3-oxy-naphthoic acid (B. **35,** 4419). **3, 4-Dimethoxy-phenanthrene-8-carboxylic acid,** m.p. 196°, has been obtained from apo-morphin, a transformation product of morphin (*q.v.*), by methylation and decomposition (B. **40,** 1998).

Hydro-phenanthrenes.—By reduction of phenanthrene with sodium and amyl alcohol, or by hydrogen in the presence of finely divided nickel, colloidal platinum, or palladium, as well as heating with HI and phosphorus, we obtain **9, 10-dihydro-phenanthrene** $C_{14}H_{12}$, m.p. 94°, b.p. 313°. **Tetra-, hexa-, octo-, deca-, dodeca-,** and **per-hydro-phenanthrene** $C_{14}H_{14}$, $C_{14}H_{16}$, $C_{14}H_{18}$, $C_{14}H_{20}$, $C_{14}H_{22}$, and $C_{14}H_{24}$, b.p. 310°, 306°, 280°–285°, 275°, 269°, and 270°–275° (B. **41,** 1000, 4225; C. 1905, I. 1396; 1911, I. 651).

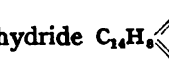
Derivatives of the 9, 10-dihydro-phenanthrene are found in the ditertiary glycols obtained by the action of alkyl- and aryl-magnesium haloids upon phenanthraquinone ditertiary glycol: **9, 10-dimethyl-, diethyl-,** and **diphenyl-9, 10-dioxy-dihydro-phenanthrene** $(C_6H_4)_2\langle^{C(OH)R}_{C(OH)R'}$ m.p. 164°, 122°, and 179°. By HI and phosphorus they are reduced to 9, 10-dialkyl-phenanthrenes, and by chromic acid they are oxidised to **o, o'-diacyl-diphenylene** $(C_6H_4)_2\langle^{COR}_{COR}$, from which, by reduction, the original glycols, or other stereo-isomeric forms, are regenerated. On heating with dehydrating agents they undergo pinacolin transposition and form **10, 10-dialkyl-phenanthrones** $(C_6H_4)_2\langle^{CO}_{CR_2}$, (?) **10, 10-dimethyl-, diethyl-,** and **diphenyl-phenanthrone,** m.p. 75°, 65°, and 198°, (cp. also 10, 10-Diphenylene-phenanthrone) (A. **362,** 242; B. **37,** 2887; C. 1905, I. 878).

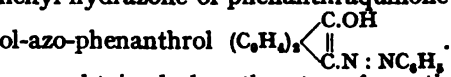
Phenanthraquinone $(C_6H_4)_2(CO)_2$ is formed in the action of chromic acid upon phenanthrene in glacial acetic acid solution; most readily by heating it with a chromic acid mixture (A. **196,** 38). It crystallises in long, orange-yellow needles, melts at 198°, and distils without decomposition. It dissolves readily in hot alcohol, ether, and benzene, but sparingly in water. It dissolves in concentrated sulphuric acid with a dark-green colour, and is reprecipitated by water. By adding toluene containing thiotolene and sulphuric acid to the acetic acid solution of phenanthraquinone a bluish-green coloration is produced (see Thiophene).

In behaviour it recalls **β-naphtho-quinone.** It is odourless, not

volatile in steam, unites with one and two molecules of hydroxylamine, and is not reduced by sulphuric acid.

Phenanthraquinone-monoxime $C_{14}H_8O(N.OH)$ consists of golden-yellow needles, melting at 158°. If it is heated together with glacial acetic acid and hydrochloric acid to 130° it sustains the transposition of ketoximes, and forms **diphenimide** (B. **21**, 2356) :

The **dioxime** forms an anhydride  , melting at 181°. This is a furazane derivative.

The monophenyl-hydrazone of phenanthraquinone is identical with the 9, 10-benzol-azo-phenanthrol  . Also, the acyl-phenyl-hydrazones obtained by the transformation of as-acetyl- and benzoyl-phenyl-hydrazin with phenanthraquinones pass spontaneously into the isomeric O-acyl-compounds of 9, 10-benzol-azo-phenanthrol (A. **378**, 211).

Phenanthraquinone, being an o-diketone, forms phenazin derivatives with o-diamines. See B. **24**, R. 630, 631, for the condensations of aceto-acetic ester and acetone. By oxidation with chromic acid, or by boiling with alcoholic potash, phenanthraquinone is oxidised to diphenic acid ; ignition with soda-lime produces *diphenylene-ketone*, *fluorene*, and diphenyl. *Diphenylene-glycollic acid*, *fluorene alcohol*, and *diphenylene-ketone* are obtained on boiling with aqueous soda-lye. Ignition with zinc dust produces phenanthrene.

By sulphurous acid, or hydrogen sulphide, it is reduced to phenanthrene-hydroquinone, by HI to phenanthrone. With HI and phosphorus in glacial acetic acid we obtain aceto-phenanthrene-hydroquinones $C_{14}H_8(OH)(OCOCH_3)$, m.p. 78° (B. **26**, R. 585 ; C. 1897, II. 1072). Mixtures of phenanthrene and quinone in sunlight give acidyl-phenanthrene-hydroquinones (A. **249**, 137). With phenol it can be condensed to phenoxy-phenanthrene-hydroquinone (C. 1900, II. 360).

Bromine acts upon phenanthrene-quinone at low temperatures with formation of an addition product $C_{14}H_8O_2Br_2$ (B. **37**, 3556). At 100° substitution products are formed : **2-bromo-** and **2, 7-dibromo-phenanthrene-quinone**, m.p. 234° and 323°. **3-** and **4-bromo-phenanthrene-quinone**, m.p. 286° and 126°, have been obtained from 3, 9- and 4, 9-dibromo-phenanthrene ; **2-chloro-phenanthrene-quinone**, m.p. 236°, from 2, 9, 10-trichloro-phenanthrene by oxidation with CrO_3 (B. **37**, 3551 ; **39**, 3893).

By heating with nitric acid, phenanthrene-quinone is converted into **2-** and **4-nitro-phenanthrene-quinone** $C_{14}H_7(NO_2)O_2$, m.p. 257° and 180°, and after prolonged action into **2, 7-** and **4, 5-dinitro-phenanthrene-quinone** $C_{14}H_6(NO_2)_2O_2$, m.p. 300°–303° and 228°. **3-Nitro-phenanthrene-quinone**, m.p. 275°, is formed from 9-bromo-phenanthrene, as well as from 9, 10-diacetamido-phenanthrene with nitric acid (B. **41**, 3679). By oxidation with chromic acid mixture nitro-phenanthrene-quinones yield nitro-diphenic acids ; by means of reduction, *amido-phenanthrene-quinones* have been obtained, and from these oxy-

phenanthrene-quinones (B. **36**, 3726; A. **322**, 135). The latter also result from acidulated phenanthrols by oxidation with CrO_3: **3-oxy-phenanthrene-quinone** $C_{14}H_7(OH)O_2$, in needles resembling alizarin and capable of sublimation; **2-oxy-phenanthrene-quinone**, dark violet needles, m.p. 280°–283°; **4-oxy-phenanthrene-quinone**, red powder, m.p. 285° (B. **44**, 740). **3, 4-Dioxy-phenanthrene-quinone**, *morphol-quinone* $C_{14}H_6(OH)_2O_2$ (diaceto-compound, m.p. 196°) has been obtained from 3-oxy-phenanthrene-quinone by way of the nitro- and amido-compounds (B. **41**, 3696).

3-Phenanthrene-quinone-sulphonic acid $C_{14}H_7O_2(SO_3H)$ from 3-phenanthrene-sulphonic acids with CrO_3 (A. **321**, 339).

Retene or 1-methyl-7-iso-propyl-phenanthrene $CH_3[1]C_6H_3\langle\begin{matrix}C_6H_3[7]C_3H_7\\CH:CH\end{matrix}\rangle$, melting at 98° and boiling at 394°, is a homologue of phenanthrene.

Retene occurs in the tar of highly resinous pines, and in some mineral resins. It is isolated from those portions that boil at elevated temperatures.

It results from the distillation of abietic acid (probably a deka-hydro-retene-carboxylic acid) with sulphur (B. **36**, 4200). Its picrate forms orange-yellow needles, melting at 123°. Chromic acid in glacial acetic acid solution oxidises retene to **retene-quinone** $C_{18}H_{16}O_2$ (*methyl-iso-propyl-phenanthraquinone*), melting at 197°. It resembles phenanthraquinone in its entire behaviour. Sodium hydrate converts retene-quinone into:

Retene-diphenic acid $C_{16}H_{16}\langle\begin{matrix}CO_2H\\CO_2H\end{matrix}$ and **retene-glycollic acid** $C_{16}H_{16}\cdot C(OH).CO_2H$. Potassium permanganate oxidises retene-quinone to **retene-ketone** $CH_3[1]C_6H_3\langle\begin{matrix}C_6H_3[7]C_3H_7\\CO\end{matrix}\rangle$, *7-oxy-iso-propyl-diphenylene-ketone-1-carboxylic acid* $CO_2H[1]C_6H_3\langle\begin{matrix}C_6H_3[7]C(OH)(CH_3)_2\\CO\end{matrix}\rangle$, and *diphenylene-ketone-1, 7-dicarboxylic acid* $CO_2H[1]C_6H_3\langle\begin{matrix}C_6H_3[7]CO_2H\\CO\end{matrix}\rangle$ the latter, in turn, passing into a mixture of 1, 2, 3- and 1, 2, 4-benzol-tricarboxylic acid. The 7-oxy-iso-propyl-diphenylene-ketone-1-carboxylic acid can be broken down to **p-iso-propyl-diphenyl** $C_6H_5.C_6H_4[4]C_3H_7$ by means of KOH, reduction with HI, and rejection of the carboxyls, which proves the position of the side-chains in retene (C. 1910, I. 1530).

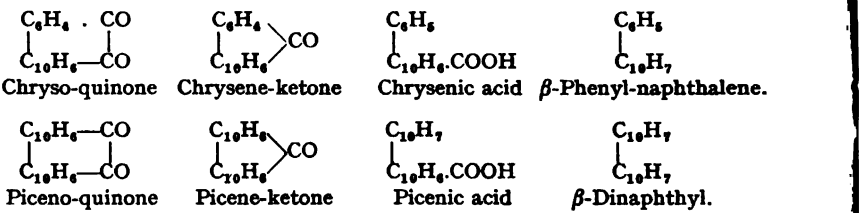
Retene dodeca-hydride, *dehydro-fichtelite* $C_{18}H_{30}$ is an oil, boiling at 336°. It is formed when retene is heated with hydriodic acid and phosphorus to 250°, and also in the action of iodine upon **fichtelite** $C_{18}H_{32}$, melting at 46°, which occurs, together with retene, in the peat of fossil plants (B. **22**, 498, 635, 780, 3369).

Chrysene and **picene** possess a structure similar to that of phenanthrene. They can be derived from phenyl-naphthalene and dinaphthyl the same as phenanthrene from diphenyl:

C_6H_4—CH	C_6H_4—CH	$C_{10}H_6$—CH
C_6H_4—CH	$C_{10}H_6$—CH	$C_{10}H_6$—CH
Phenanthrene	Chrysene	Picene.

The constitution of these bodies is deduced mainly from the pro-

ducts of their oxidation. Chromic acid first changes them to chryso-quinone and piceno-quinone, which can be further transposed into chrysene- and picene-ketones, chrysenic acid and picenic acid, β-phenyl-naphthalene and β-dinaphthyl :



Chrysene $C_{18}H_{12}$, m.p. 250° and b.p. 448°, consists, in a pure condition, of silver-white flakes with a violet fluorescence. When impure it has a yellow colour (hence the name from χρύσεος, gold-yellow). It occurs in those portions of coal-tar which have high boiling-points. It can be synthesised from phenyl-naphthyl-ethane $C_6H_5.CH_2.CH_2.C_{10}H_7$, just as phenanthrene is produced from dibenzyl ; also by heating naphthalene with cumarone. It is formed in large quantities by heating indene $2C_9H_8=C_{18}H_{12}+4H$ (B. **26**, 1544). See B. **24**, 949, for substituted chrysenes. The *hydrides*, $C_{18}H_{28}$, b.p. 360°, and $C_{18}H_{30}$, m.p. 115° and b.p. 353° (B. **22**, 135), result upon heating chrysene with hydriodic acid and phosphorus.

When digested with chromic acid and glacial acetic acid chrysene oxidises to so-called **chryso-quinone** $C_{18}H_{10}O_2$ (a diketone), which crystallises in red needles, melting at 235°.

Chryso-ketone $C_{17}H_{10}O$ results when chryso-quinone is distilled with lead oxide. Hydriodic acid and phosphorus reduce it to chryso-fluorene $C_{17}H_{12}$.

On boiling with permanganate, chrysene-quinone, and chrysene-ketone even more readily, give diphthalic acid $COOHC_6H_4CO.COC_6H_4COOH$. On heating with soda-lime or potash and PbO_2, chrysene-quinone yields chrysenic acid or β-phenyl-α-naphthoic acid, which by rejection of CO_2 yields β-phenyl-phthalin (B. **26**, 1745). A transposition of chrysene-quinone-oxime $C_{16}H_{10}\begin{cases}C:NOH\\CO\end{cases}$, m.p. 161°, produces at 100° two isomeric amido-acids $C_{16}H_{10}\begin{cases}COOH\\CONH_2\end{cases}$, m.p. 220° and 275°, which on saponification give **chryso-diphenic acid** $\begin{matrix}C_6H_4COOH\\|\\C_{10}H_6COOH\end{matrix}$, m.p. 199°, and, in the manner of diphenaminic acid, are converted by sodium hypochlorite into α- and β-naphthanthridone $\begin{matrix}C_{10}H_6.NH\\C_6H_4.CO\end{matrix}$, m.p. 332°, and $\begin{matrix}C_{10}H_6.CO\\C_6H_4.NH\end{matrix}$, m.p. 338° (A. **311**, 257 ; **335**, 124 ; B. **35**, 2744).

Picene $C_{22}H_{14}$ is the hydrocarbon with the highest melting-point (364°). It is formed by the distillation of lignite, coal-tar, and petroleum residues. It can be synthesised from naphthalene and ethylene bromide by means of $AlCl_3$ (B. **24**, R. 963 ; **32**, 3341 ; C. 1910, II. 471). It is very sparingly soluble in most solvents, but most readily in crude cymol. When heated to 250° with hydro-iodic acid and phosphorus,

picene-perhydride $C_{22}H_{36}$ is produced. It melts at 175°. Picene is oxidised by chromic acid to an orange-red *quinone* $C_{22}H_{12}O_2$, which, like chrysene, is changed on the one hand to *picene-ketone*, *picene-fluorene alcohol*, and picene-fluorene $(C_{10}H_6)_2CH_2$, and on the other to *picenic acid* or *dinaphthyl-carboxylic acid* and β-dinaphthyl (B. **26**, 1751).

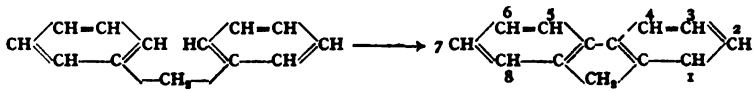
Pyrene $C_{16}H_{10}$, lemon-yellow plates, m.p. 149°, b.p.$_{60}$ 260°; picrate, m.p. 222°; it is converted, by chromic acid in glacial acetic acid, into **pyrene-quinone** $C_{16}H_8O_2$, and on further oxidation to **pyrenic acid** $C_{12}H_6(CO)(COOH)_2$ (M. **31**, 861), a ketone-dicarboxylic acid which easily shows anhydride and imide formations (B. **19**, 1997), and, on distillation, produces **pyrene-ketone** $C_{12}H_8(CO)$, m.p. 141°. On oxidising pyrenic acid with MnO_4K, we obtain 1, 4, 5, 8-naphthalene-tetracarboxylic acid, and from pyrene-ketone naphthalic acid. On the constitutions of pyrene, as one of the ring systems consisting of four condensed benzene nuclei, see B. **20**, 365; A. **351**, 218.

Triphenylene $\begin{matrix}C_6H_4.C{-}CH{=}CH\\ C_6H_4.C{-}CH{=}CH\end{matrix}$, white needles, m.p. 198°, is formed on conducting benzene vapours through incandescent tubes. Fuming nitric acid oxidises it to mellithic acid. A **dodeca-hydro-triphenylene** $C_{18}H_{24}$, m.p. 233°, is formed by the condensation of cyclo-hexanone with alcoholic H_2SO_4, as mesitylene from acetone (B. **40**, 153). See also **tricyclo-trimethylene benzol** $C_{15}H_{12}$, m.p. 96° (B. **30**, 1094).

IV. Fluorene Group.

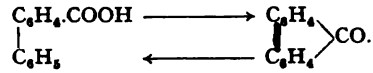
Just as phenanthrene, chrysene, and picene were regarded as symmetrical o_2-ethylene derivatives of diphenyl, phenyl-naphthyl, and dinaphthyl, so *fluorene*, *chrysene-fluorene*, and *picene-fluorene* may be viewed as o_2-methylene derivatives of the last-mentioned hydrocarbons, and accordingly may be designated *diphenylene-methane*, *phenylene-naphthylene*, and *dinaphthylene-methanes*. On the other hand, they can, like indene, be regarded as condensed cyclo-pentadiene derivatives: dibenzo-, benzo-naphtho-, and dinaphtho-cyclo-pentadiene. Fluorene is also closely allied to diphenylene oxide, diphenylene sulphide, and diphenylene-imide or carbazol (*q.v.*), dibenzo-derivatives of furfurane, thiophene, and pyrrol:

General Methods of Formation.—1. Fluorene is formed by conducting vapours of diphenyl-methane through tubes heated to redness; chryso-fluorene is similarly obtained from β-naphthyl-phenyl-methane:

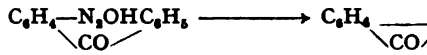


2. o-Diphenyl-carboxylic acid, phenyl-naphthyl-carboxylic acid or chrysenic acid, and dinaphthyl-carboxylic or picenic acid, when heated alone or in the form of salts, yield fluorene-, chrysene-, and picene-

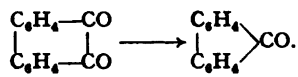
ketones, which can be readily reduced to fluorene, chryso-fluorene, and picene-fluorene; conversely, the acids are reformed when the ketones are fused with caustic potash:



3. Fluorene-ketone is also obtained from the diazo-derivative of o-amido-benzo-phenone by the elimination of nitrogen; similarly, chrysene-ketone is formed from o-amido-phenyl-α-naphthyl-ketone (B. **29**, 826):



4. Phenanthraquinone, chryso-quinone, and piceno-quinone, when oxidised, also yield the ketones of the corresponding fluorenes:



Fluorene, *diphenylene-methane* $C_{13}H_{10}$, m.p. 113° and b.p. 295°, crystallises in colourless leaflets with a violet fluorescence. It forms a compound with picric acid, melting at 81°.

It is found in coal-tar (fraction 270°–300°); on heating with sodium or sodium amide to 120°–150°, it forms a sodium salt $(C_6H_4)_2 : CHNa$, by means of which it can be detached from the accompanying hydrocarbons (B. **41**, 2913).

It results upon exposing diphenyl-methane to a high temperature (above), and in the reduction of diphenylene-ketone with zinc dust or upon heating it to 160° with HI and phosphorus. The chromic acid mixture oxidises it to diphenylene-ketone.

In fluorene the hydrogen atoms of the CH_2 group are mobile as in cyclo-pentadiene and indene, but to a less extent. Heating with caustic potash and benzyl chloride forms **dibenzyl-fluorene** $(C_6H_4)_2C(CH_2C_6H_5)_2$, m.p. 148°; with benzaldehyde, cinnamic aldehyde, etc., it condenses to colourless or faintly coloured **benzylidene-fluorene** $(C_6H_4)_2C : CHC_6H_5$, m.p. 76°, and **cinnamylidene-fluorene** $(C_6H_4)_2C : CH.CH : CHC_6H_5$, m.p. 154°; with oxalic ester to **fluorene-oxalic ester** $(C_6H_4)_2CHCOCO_2C_2H_5$, m.p. 75°; with formic ester to formyl-fluorene or diphenyl-acetaldehyde $(C_6H_4)_2CH.CHO$, m.p. about 70° (B. **43**, 2719); with amyl nitrite and ethyl nitrate under the influence of potassium ethylate free from alcohol, it yields **fluorenone-oxime** $(C_6H_4)_2C : NOH$ and **9-nitro-fluorene** $(C_6H_4)_2CHNO_2$ respectively, which, like phenyl-nitro-methane, occurs in an acid form soluble in alkalies, m.p. 135°, and a neutral form, insoluble in alkalies, m.p. 182° (A. **347**, 290; B. **33**, 852; **41**, 3334).

By reduction of fluorene with HI and phosphorus, or hydrogen and nickel, we obtain **perhydro-fluorene** $C_{13}H_{22}$, b.p. 256°–258°, D_{22} 0·9203 (B. **42**, 920, 2093). The isolation of a **hexahydro-fluorene** $C_{13}H_{16}$, from coal, by extraction with benzene, or distillation in a vacuum, is noteworthy (B. **44**, 2486).

By bromination of fluorene in boiling chloroform we obtain **2, 7-dibromo-fluorene** $C_{13}H_8Br_2$, m.p. 164°, and **2, 6**(?), **7-tribromo-fluorene**

$C_{13}H_7Br_3$, m.p. 200° (B. **38**, 3764). 9-Chloro-fluorene $C_{13}H_9Cl$, m.p. 90° from fluorene alcohol with PCl_5 (B. **37**, 2896).

Nitration of fluorene in glacial acetic acid produces **2-nitro-fluorene** $NO_2—C_{13}H_9$, m.p. 153°, which, by known methods, can be converted into **2-amido-diazo-** and **oxy-fluorene** and **2-fluoryl-hydrazin.** Nitration of the 2-acetamido-fluorene produces **2, 7-** and **2, 1-amido-nitro-fluorene,** m.p. 232° and 206°, which produce **2, 7-** and **2, 1-diamido-fluorene,** m.p. 164° and 193° (B. **34**, 1758; **35**, 3284); **9-amido-fluorene,** two modifications, m.p. 54° and 123°, by reduction of fluorenone oxime (B. **41**, 1243).

Retene - fluorene, 1 - *methyl* - 7 - *iso* - *propyl* - *diphenyl* - *methane* $\begin{matrix}(CH_3)C_6H_3\\(C_3H_7)C_6H_3\end{matrix}\!\!>\!CH_2$, melting at 97°, is derived from its ketone upon distillation with zinc dust. **Chryso-fluorene,** *naphthylene-phenylene-methane* $C_{10}H_6—CH_2—C_6H_4$, melting at 180°, is derived from β-benzyl-naphthalene or from chryso-ketone. An **iso-naphtho-fluorene** $\begin{matrix}\beta C_{10}H_6[\beta]\\C_6H_4\text{——}\end{matrix}\!\!>\!CH_2$, m.p. 208°, has been obtained from iso-naphtho-fluorenone (A. **376**, 276; B. **27**, 953). **Picene-fluorene,** *picylene-methane* $(C_{10}H_8)_2CH_2$, melting at 306°, is produced on heating its ketone to 160°–175° with hydriodic acid (A. **284**, 70).

This is isomeric with the αα- and ββ-dinaphtho-fluorene, m.p. 236° and 186°, obtained from αα- and ββ-dinaphthyl carbinol (B. **43**, 2832).

Methyl-hexahydro-fluorene, boiling at 128° (14 mm.), results from the action of P_2O_5 upon methyl-benzyl-cyclo-hexanol, the reduction product of benzylidene-methyl-cyclo-hexanone $(CH_3)(OH)C_6H_9 : CH_2.C_6H_5$ ⟶ $(CH_3)C_6H_9.CH_2.C_6H_4$ (B. **29**, 2962; A. **305**, 264).

Diphenylene-phenyl-methane, *phenyl-fluorene* $(C_6H_4)_2CHC_6H_5$, melting at 146°, results (1) on heating triphenyl-methane chloride $(C_6H_5)_3CCl$, or potassium-triphenyl-methane; (2) from triphenyl-carbinol by distillation with crystallised phosphoric acid; (3) from fluorene alcohol, benzene-sulphuric acid; (4) from 9-chloro-fluorene, benzene, and $AlCl_3$ (5) from hydro-fluoranic acid by distillation over soda-lime; and (6) by reduction of **diphenylene - phenyl - carbinol,** 9 - *phenyl* - *fluorenol* $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!C\!<\!\begin{matrix}OH\\C_6H_5\end{matrix}$, m.p. 107°. The latter, analogous to triphenyl-carbinol, is obtained from diphenylene-ketone with phenyl-magnesium bromide, or by oxidation of 9-phenyl-fluorene with chromic acid; it gives intensely coloured double salts and perchlorate; with aniline chlorohydrate it condenses to **diphenylene-p-amido-diphenyl-methane** $(C_6H_4)_2C(C_6H_5)C_6H_4NH_2$, m.p. 179°; with phenol and sulphuric acid to **diphenylene-p-oxy-diphenyl-methane,** m.p. 191° (B. **37**, 73). By the action of PCl_5, acetyl chloride, or gaseous HCl, it passes into **9, 9-phenyl-chloro-fluorene** $(C_6H_4)_2CClC_6H_5$, m.p. 79°, which, like triphenyl-chloro-methane, is distinguished by the mobility of its chlorine atom. By heating with copper powder in benzene solution it passes into **di-biphenylene-diphenyl-ethane** $(C_6H_4)_2(C_6H_5)C.C(C_6H_5)(C_6H_4)_2$, m.p. 254°. This forms colourless crystals which dissolve colourless in the cold, and only assume a dark-brown colour on heating, with partial decomposition into two molecules **biphenylene-phenyl-methyl** $(C_6H_4)_2C(C_6H_5)$. In the air it absorbs oxygen, and accordingly passes into

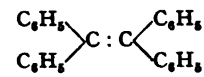
the corresponding peroxide, m.p. 193°. Still more stable is the analogous body **di-biphenylene-di-biphenyl-ethane** $(C_6H_4)_2(C_6H_5.C_6H_4)C.C(C_6H_4.C_6H_5)(C_6H_4)_2$, m.p. 176°, obtained from **9, 9-biphenyl-chloro-fluorene** $(C_6H_4)_2CClC_6H_4.C_6H_5$, m.p. 139°, which only undergoes a slight dissociation in boiling anisol and is insensitive to oxygen, both in solution and in the solid state (A. **372,** 21 ; B. **43,** 1753).

Phenyl-chryso-fluorene $\begin{matrix}C_{10}H_6\\C_6H_4\end{matrix}\!\!>\!CHC_6H_5$, m.p. 195°, from diphenyl-α-naphthyl-carbinol with concentrated SO_4H_2 or $ZnCl_2$ (B. **38,** 2215) ; **9, 9-diphenyl-fluorene** $(C_6H_4)_2C(C_6H_5)_2$, m.p. 220°, analogous to diphenyl-monobiphenyl-carbinol (B. **38,** 4105).

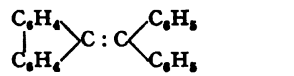
Diphenylene-diphenyl-ethane $(C_6H_4)_2CH.CH(C_6H_5)_2$, melting at 217°, and **diphenylene-diphenyl-ethylene** $(C_6H_4)_2C:C(C_6H_5)_2$, melting at 229°, arise in the breaking-down of *diphenylene-diphenyl-succinic anhydride* $\begin{matrix}(C_6H_4)_2.C.CO\\(C_6H_5)_2.C.CO\end{matrix}\!\!>\!O$, melting at 256°, one of the reaction products of cold concentrated sulphuric acid upon benzilic acid. Diphenylene-diphenyl-ethylene is produced on heating benzo-phenone chloride with fluorene. It consists of *colourless* crystals, the solutions of which are *coloured intensely yellow.* The moderated oxidation of this body with chromic acid gives rise to **9, 9-benzoyl-phenyl-fluorene** $(C_6H_4)_2C(C_6H_5)COC_6H_5$, m.p. 172°, by pinacolin transformation from the pinacone first formed. It is also obtained from potassium-triphenyl-methane, or potassium-9-phenyl-fluorene with benzoyl chloride. Alcoholic potash breaks it up into 9-phenyl-fluorene and benzoic acid. By reduction with HI and phosphorus, benzoyl-phenyl-fluorene is converted into 9, 10-diphenyl-phenanthrene, with reversal of the pinacolin transposition and expansion of the ring (B. **37,** 2887).

Bi-diphenylene-ethane $(C_6H_4)_2CH.CH(C_6H_4)_2$, colourless needles, melting at 246°, is produced, together with **bi-diphenylene-ethylene,** *bifluorene* $(C_6H_4)_2C:C(C_6H_4)_2$, melting at 188°, on heating fluorene with lead oxide. The second hydrocarbon is also formed on heating fluorene with bromine, chlorine, or sulphur, and by the action of alcoholic potash upon 9-bromo-fluorene (A. **376,** 271) ; or of copper powder upon fluorene dichloride (B. **43,** 1796).

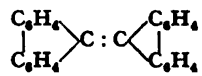
It consists of beautiful *red*-coloured needles. Its bromine addition product is colourless, and when heated with sodium in xylene solution it reverts to the red hydrocarbon (B. **25,** 3140 ; A. **290,** 238 ; **291,** 1). The following diagram is interesting from the point of view of the colour of highly condensed hydrocarbons :



Tetraphenyl-ethylene. Colourless



Diphenylene-diphenyl-ethylene. Colourless ; yellow in solution



Bi-diphenylene-ethylene. Red needles.

Compare the yellow colour of acenaphthylene and the red colour of diphenyl-fulvene. On oxidation with chromic acid the di-biphenylene-ethylene forms, by a change analogous to the pinacolin transposition, besides fluorenone, a **10, 10 - diphenylene - phenanthrone** $(C_6H_4)_2:C{-}C_6H_4$ (?), m.p. 258°, which is broken up by alcoholic
$\quad\quad\quad

potash to form the acid $(C_6H_4) : CH—C_6H_4.C_6H_4COOH$. The same pinacolin is also formed in the reduction of fluorenone with zinc dust and acetyl chloride. It is probably identical with the so-called di-biphenylene-ethylene oxide obtained from di-biphenylene-ethylene dibromide by heating with water. By reduction with HI it is transformed into **9, 10-diphenylene-phenanthrene** $\begin{matrix}C_6H_4.CH.C_6H_4\\C_6H_4.CH.C_6H_4\end{matrix}$ (?) m.p. 215°, with another transposition (B. **29**, 2152 ; **37**, 2894 ; A. **291**, 1).

Fluorene alcohol, *fluorenol* $(C_6H_4)_2CHOH$, m.p. 153°, is formed from the ketone with Na amalgam and from the Na salt of diphenyl-glycolic acid by heating to 120°. Like fluorene alcohol, retene, picene, and chrysene-fluorene alcohols, m.p. 134°, 167°, and 230°, are obtained. *Fluorene ether* $[(C_6H_4)_2CH]_2O$, m.p. 228°, from 9-chloro-fluorene and Ag_2O (B. **48**, 2490). Methyl-, ethyl-, and benzyl-fluorenol $(C_6H_4)_2C(OH)R$, m.p. 174°, 101°, and 139°, are formed from fluorenone with the corresponding alkyl Mg haloids (B. **38**, 4105).

Diphenylene-ketone, *fluorenone* $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>\!CO$, melting at 84° and boiling at 341° (B. **27**, R. 641), is obtained from diphenic acid, iso-diphenic acid, and o-diphenyl-carboxylic acid when heated with lime ; by oxidising fluorene with a chromic acid mixture, and by heating phenanthraquinone with caustic lime (A. **196**, 45 ; **279**, 257), and when the diazo-compound of o-amido-benzo-phenone is heated with water (B. **28**, 111). Potassium permanganate oxidises it to phthalic acid. It is converted into o-phenyl-benzoic acid on fusion with potassium hydroxide. Its *oxime* $(C_6H_4)_2C : NOH$ melts at 193° ; the *phenyl-hydrazone* melts at 151° (B. **29**, 230, R. 26).

Retene-ketone $(C_3H_7)(CH_3)\overline{C_6H_2.CO.C_6H_4}$ melts at 90°. **Chryso-ketone,** *naphtho-fluorenone* $\overline{C_6H_4.CO.C_{10}H_6}$, melts at 130°. On the formation of the latter from o-amido-phenyl-α-naphthyl-ketone, see above. An **iso-naphtho-fluorenone,** m.p. 152°, has been obtained by condensation from o-phthalaldehyde with α-hydrindone by means of K methylate (A. **376**, 269). **Picene-ketone** $(C_{10}H_6)_2CO$, m.p. 185° ; *αα*- and *ββ*-**dinaphtho-fluorenone,** m.p. 225° and 161°, from the corresponding dinaphtho-fluorenes (B. **48**, 2833).

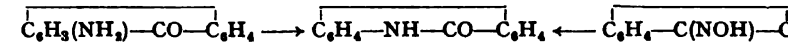
With concentrated HNO_3 in the cold, fluorenone yields a loose addition product $(C_6H_4)_2CO.NO_3H$, which easily separates into its components. Energetic nitration gives **2, 7-dinitro-** and **2, 6, 7-trinitro-fluorenone,** m.p. 290° and 181° respectively (B. **38**, 3758).

o-Oxy-diphenylene-ketone, *oxy-fluorenone* $\overline{C_6H_3(OH).CO.C_6H_4}$, melting at 115°, is obtained from sym. o-diamido-benzo-phenone on boiling its diazo-salts with water, together with xanthone (B. **31**, 3034) ; and from **1-amido-diphenylene-ketone,** m.p. 110°, obtained from diphenylene-ketone-1-carboxylic amide with KOBr (C. 1902, II. 1472). The 1-oxy-fluorenone forms yellowish-red or dark-red alkali salts, showing feeble drying properties.

When fused with caustic potash it decomposes into o-phenyl-salicylic acid $C_6H_5.C_6H_3(OH)COOH$, which is recondensed by concentrated sulphuric acid to oxy-diphenylene-ketone (B. **23**, 112). 4-Oxy-diphenylene-ketone is also prepared from **4-amido-diphenylene-ketone,**

melting at 138°, which is obtained from diphenylene-ketone-carboxyl-amide with bromine and caustic potash.

By fusing with potash the 4-amido-fluorenone is transformed into phenanthridone (B. **28**, R. 455), which also results by Beckmann's transposition on heating the oxime of fluorenone with zinc chloride (B. **29**, 230) :



4-Amido-fluorenone — Phenanthridone — Fluorenone-oxime.

2-Amido-fluorenone, m.p. 163°, from **2-nitro-fluorenone**, m.p. 222°–223°, the oxidation product of 2-nitro-fluorene, by reduction with Am_2S, gives with the diazo-salts **2-oxy-fluorenone**, m.p. 210°–211° (B. **34**, 1764). **3-Oxy-fluorenone**, m.p. 229°, is formed from synthetic 3-oxy-fluorenone-4-carboxylic acid by splitting off CO_2.

Carboxylic Acids.—**Diphenylene-acetic acid**, *fluorene-carboxylic acid* $(C_6H_4)_2CH.CO_2H$, melting at 221°, results on reducing diphenylene-glycollic acid with hydriodic acid and phosphorus. Also from trichlor-acetic ester with benzene and $AlCl_3$ (C. 1902, II. 991). Its nitrile, m.p. 152°, is formed from diphenylene-acetaldoxime with acetyl chloride.

Diphenylene-glycollic acid, ms-oxy-fluorene-carboxylic acid $(C_6H_4)_2C(OH).CO_2H$, melting at 162°, is produced when phenanthraquinone is boiled with sodium hydroxide. In this instance an atomic rearrangement occurs, similar to that observed in the transition of benzile to benzilic acid, or of β-naphtho-quinone to oxy-indene-carboxylic acids :

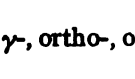
Chromic acid oxidises it to diphenylene-ketone. Analogues of diphenylene-glycollic acid have been obtained from retene- and chrysene-quinone (above), and from other substituted phenanthrene-quinones (B. **38**, 3737). With phenols and phenol ethers diphenylene-glycollic acid condenses in the manner of benzilic acid, under the influence of tin tetrachloride, to form substituted diphenylene-phenyl-acetic acids (B. **48**, 2496). With PCl_5 it forms diphenylene-chloro-acetic-acid chloride, m.p. 112°, which, on treatment with zinc chips in ether solution, passes into **diphenylene-ketene** $(C_6H_4)_2C : CO$, golden-yellow spears, m.p. 90°, an analogue of diphenyl-ketene (B. **39**, 3062).

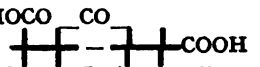
Fluorene-oxalic acid $(C_6H_4)_2CH.COCOOH + H_2O$, m.p. 150°–151°, decomposes on heating into CO, CO_2, and fluorene ; its esters, formed from fluorene, oxalic ester, and sodium, give, with Na alcoholate and ICH_3 or IC_2H_5, methyl- and ethyl-fluorene-oxalic esters, and, by splitting up the latter, **9-methyl-fluorene** $(C_6H_4)_2CHCH_3$, m.p. 46°–47°, and **9-ethyl-fluorene** $(C_6H_4)_2CHC_2H_5$, m.p. 108°, b.p.$_{18}$ 166° (B. **35**, 759).

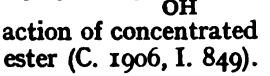
Diphenylene-ketone-carboxylic acids, or 1-acid .

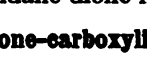
The *α-acid*, melting at 191°, is produced by the oxidation of fluoranthene with a chromic acid mixture. Sodium amalgam converts it into *α-fluorenic acid* $C_6H_4.CH_2.C_6H_3.CO_2H$, melting at 245°, which yields fluorene if it be distilled with zinc dust. Iso-diphenic acid results

when it is fused with potassium hydroxide, while heating with lime breaks it down into carbon dioxide and diphenylene-ketone.

The γ-, ortho-, or 4-acid  is formed when diphenic acid is heated. It melts at 227°. Fusion with caustic potash changes it to diphenic acid (B. **20,** 846; **22,** R. 727). Also from diphenic anhydride with $AlCl_3$ in benzene, besides o-benzoyl-fluorenone, m.p. 95° (C. 1902, I. 875).

Diphenylene-ketone-1, 7-dicarboxylic acid  is formed from retene-quinone (above) with MnO_4K. It is a yellow powder, decomposing at 270° into CO_2 and **diphenylene-ketone-2-carboxylic acid,** m.p. 275°. Distilled with lime it forms diphenyl. On heating its silver salt it forms diphenylene-ketone, and, on further oxidation with MnO_4K, a mixture of 1, 2, 3- and 1, 2, 4-benzol-tricarboxylic acid (A. **229,** 158; C. 1904, II. 449; 1910, I. 1530).

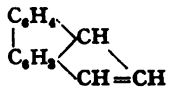
3-Oxy-diphenylene-ketone-2-carboxylic acid  , m.p. 278°, is formed by nuclear synthesis in the action of concentrated potash upon indane-dione-methenyl-aceto-acetic ester (C. 1906, I. 849).

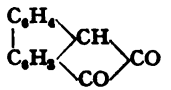
Chryso-ketone-carboxylic acid  , m.p. 283°, is formed, besides small quantities of an isomeric acid, by the action of concentrated SO_4H_2 upon chryso-diphenic acid (A. **335,** 119). A third isomeric **allo-chryso-ketone-carboxylic acid,** m.p. 288°, has been obtained by heating 1-phenyl-naphthalene-2, 3-dicarboxylic acid with concentrated H_2SO_4 (C. 1908, II. 1360).

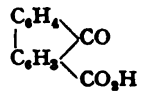
Fluoranthene and *pyrene,* occurring in the "stubb fat" of Idria, are also found with the condensed hydrocarbons just mentioned in the high boiling fractions of coal-tar.

Fluoranthene $C_{15}H_{10}$, **idryl,** melts at 110°. Its *picric acid compound* melts at 182°. **Fluoranthoquinone** $C_{15}H_8O_2$ is obtained by oxidising idryl with chromic acid. It melts at 188°, and may be further oxidised (with the elimination of CO_2) to obtain α-diphenylene-ketone-carboxylic acid.

The constitution of fluoranthene and of fluoranthoquinone probably corresponds to the formulæ (A. **200,** 1):


Fluoranthene


Fluoranthoquinone


α-Diphenylene-ketone-carboxylic acid.

Cp. also *phthalacene* $C_{20}H_{16}$ (B. **17,** 1389; C. 1908, I. 644; 1909, I. 535).

V. Anthracene Group.

Anthracene (from ἄνθραξ, carbon), occurring together with the isomeric phenanthrene in the high-boiling portions of coal-tar, is the parent substance of a large group of bodies to which a series of vegetable

compounds, and in particular the very important dye (*alizarin, purpurin*, etc.) of madder root belong.

Synthetic Methods for the Production of Anthracene Derivatives.

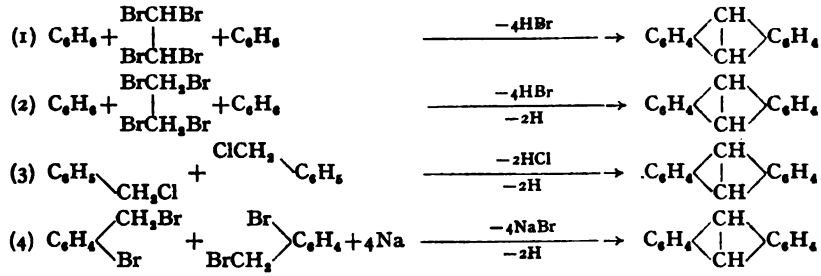
1. Anthracene may be formed from benzene, acetylene tetrabromide, and $AlCl_3$ (B. **16**, 623).

2. It is also produced from methylene bromide, benzene, and Al_2Cl_6. Dihydro-anthracene is the primary product, but it loses two atoms of hydrogen, and anthracene results.

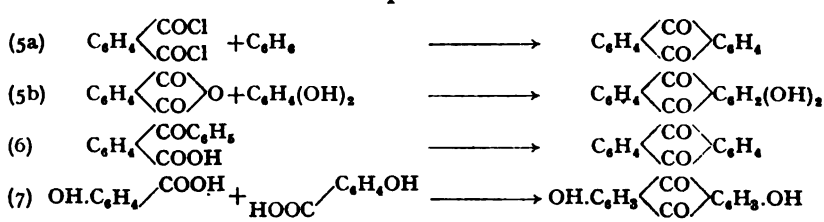
3. Further, dihydro-anthracene, and subsequently anthracene, is obtained (together with toluene) from two molecules of benzyl chloride on heating it with aluminium chloride or with water to 200° (Limpricht, 1866), when dibenzyl will also be produced.

Anthracene may also be derived from diphenyl-methane with $AlCl_3$. It is very probable that the diphenyl-methane is first resolved into benzyl chloride and benzene. Unsym. diphenyl-ethane in an analogous manner yields ms-dimethyl-anthracene (B. **27**, 3238).

4. Finally, dihydro-anthracene is obtained from two molecules of o-bromo-benzyl bromide by the action of metallic sodium (B. **12**, 1965) (cp. p. 689) :



Anthraquinones are obtained (5*a*) by the action of zinc dust upon the chloride of phthalic acid and benzene. (5*b*) Similarly, oxy-anthraquinones are produced on heating phthalic anhydride with one molecule of a mono- or polyhydric phenol and sulphuric acid to 150°. If there is an excess of phenol present, phthaleïns result. (6) o-Benzoyl-benzoic acid and P_2O_5 yield anthraquinone on the application of heat. The substituted benzoyl-benzoic acids form the substituted anthraquinones, and benzyl-benzoic acid forms anthrone. (7) Di- and tetra-oxy-anthraquinones are formed when metaoxy- and dimeta-dioxy-benzoic acids are heated with sulphuric acid :

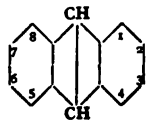


The methods just given and a series of others—*e.g.* the production of anthraquinone from o-tolyl-phenyl-ketone and lead oxide, and that of

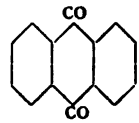
anthracene and methyl-anthracene from o-tolyl-phenyl-ketone and o-ditolyl-ketone by means of zinc dust (B. **23**, R. 198)—demonstrate the accepted symmetry of the derivatives of anthracene, which is further proved by the following fact: brominated o-benzoyl-benzoic acid from o-phthalic acid yields bromo-anthroquinone; the oxy-anthraquinone obtained from the latter, however, can be oxidised to o-phthalic acid; so that both in the synthesis and decomposition of the molecule o-phthalic acid appears, which, in the first instance, is connected with the one and in the second case with the second half of the molecule (cp. constitution of naphthalene) (B. **12**, 2124):

$$Br.C_6H_3\begin{cases}[1]CO.C_6H_5\\[2]COOH\end{cases} \longrightarrow OH.C_6H_3\begin{cases}[1]CO[1]\\[2]CO[2]\end{cases}C_6H_4 \longrightarrow \begin{matrix}HOOC[1]\\HOOC[2]\end{matrix}\Big\}C_6H_4.$$

Therefore anthraquinone and anthracene, which are genetically connected, have a symmetrical constitution corresponding to the symbols:



Anthracene



Anthraquinone.

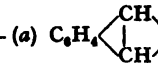
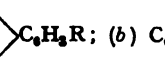
Anthracene is a nucleus resulting from the condensation of three benzene nuclei, of which the intermediate or middle member shows a para-union. The positions 1, 4, 5, 8 (*α*-) are alike; also 2, 3, 6, 7 (*β*-). By the replacement of the middle hydrogen atoms of anthracene *γ*-derivatives or *meso*-derivatives are obtained. In contrast with this the substituents of the two outer benzene nuclei are designated by the prefix *benz*. In most of the anthracene transpositions the intermediate C atoms are first attacked.

Anthracene $C_{14}H_{10}$, melting at 213° and boiling at 351°, is isomeric with phenanthrene, and is produced according to the methods indicated above. (See also B. **23**, R. 148.) It is found in large quantities in coal-tar.

Crude anthracene, boiling at 340°–360° and beyond, is best purified by treating it with liquid sulphurous acid, which chiefly takes up the admixtures (B. **26**, R. 634). For additional methods of purification, see B. **18**, 3034; **21**, R. 75; A. **191**, 288. Chemically pure anthracene is prepared by heating anthraquinone with zinc dust.

Anthracene crystallises in colourless monoclinic tables, showing a beautiful blue fluorescence. It dissolves with difficulty in alcohol and ether, but easily in hot benzene. Picric acid unites with it, yielding $C_{14}H_{10}.C_6H_2(NO_2)_2OH$, crystallising in red needles, and melting at 138°.

When the cold saturated solution of anthracene in benzene, or, better, in xylene (B. **26**, R. 547), is exposed to sunlight, a dimolecular modification of anthracene, *para-anthracene* $(C_{14}H_{10})_2$, separates out in plates. It dissolves with difficulty in benzene, is not attacked by nitric acid or bromine, melts at 244°, and, in so doing, reverts to common anthracene.

Alkylic Anthracenes. — (*a*)  (*b*) 

Benzalkyl derivatives — meso- or *γ*-Alkyl derivatives.

(*a*) The benzo-mono-alkylic anthracenes can exist in two isomerides (*α*- and *β*-).

α-Methyl-anthracene $C_6H_4(CH_2)C_6H_3[1]CH_3$, m.p. 86°, is formed by zinc dust distillation from 1, 4-chloro-methyl-anthraquinone (*J. pr. Ch.* 2, **83**, 201).

β-Methyl-anthracene $C_6H_4(CH_2)C_6H_3[2]CH_3$, m.p. 207°, closely resembles anthracene, and is found in the crude anthracene of coal-tar.

At high temperatures it is formed out of ditolyl-methane and ethane (*J. pr. Ch.* 2, **79**, 355); also by boiling benzoyl-xylol $C_6H_5CO.C_6H_3(CH_3)_2$; by reduction of *β*-methyl-anthraquinone with zinc dust (A. **311**, 181); and from vegetable *chrysophanic acid* and *emodin*, which are hydroxylated methyl-anthraquinones. By oxidation with nitric acid, methyl-anthracene forms methyl-anthraquinone, and with chromic acid mixture and oxidation of the methyl group it forms anthraquinone-carboxylic acid. In sunlight it polymerises like anthracene to dimethyl-dianthracene, m.p. 229° (C. 1899, II. 623).

1, 6- and **2, 6-Dimethyl-anthracene** $C_{14}H_8(CH_3)_2$, m.p. 240° and 244°, are formed together from toluol and methylene chloride or acetylene tetrabromide with $AlCl_3$ (method 2). The second body has also been obtained by boiling m-xylyl-tolyl-ketone (C. 1910, II. 1386; 1911, I. 1294). From the aniline oils of high boiling-point also a dimethyl-anthracene has been obtained.

(*b*) Meso- or *γ*-alkyl-anthracenes are obtained from the alkylic hydranthranols $C_6H_4\langle\begin{matrix}CR(OH)\\CH_2\end{matrix}\rangle C_6H_4$ by the elimination of water. This happens on boiling them with alcohol, hydrochloric acid, or picric acid (A. **212**, 100). Alkylic oxanthranols are formed upon oxidation: **γ-ethyl-, iso-butyl-,** and **amyl-anthracenes,** melting at 60°, 57°, and 59°. **γ-Phenyl-anthracene** $C_{14}H_9(C_6H_5)$, melting at 152°, is obtained from phenyl-anthrone.

γ- or **9, 10-Diphenyl-anthracene** $C_6H_4(C.C_6H_5)_2C_6H_4$, m.p. 240°, from diphenyl-dioxy-anthracene hydride with zinc dust and glacial acetic acid (C. 1904, II. 117; 1906, I. 44).

γ- or **9, 10-Dimethyl-anthracene** $C_6H_4(C.CH_3)_2C_6H_4$, melting at 179°, is derived from its dihydride, the condensation product obtained from ethidene chloride and benzene by means of Al_2Cl_6 (see B. **21**, 1176).

9, 10-Dibenzyl-anthracene $C_6H_4(C.CH_2C_6H_5)_2C_6H_4$, m.p. 240°, is formed by prolonged boiling of anthracene with benzyl chloride and a little zinc dust in CS_2 solution (C. 1902, II. 745; 1904, II. 1136).

Substituted Anthracenes.—Chlorine and bromine acting upon the CS_2 solution of anthracene first substitute the middle CH groups with the production of **γ-mono-** and **dihalogen-anthracenes.** γ-Dibromo-anthracene is also formed by the action of bromine upon anthracene hydride.

The action of nitric acid upon anthracene easily produces anthraquinone and nitrified anthraquinones. But on nitrifying with acetic anhydride and sulphuric acid in glacial acetic acid at 15°–20°, we obtain **9-nitro-anthracene** $C_{14}H_9.NO_2$, yellow needles, m.p. 145°–146°, which may be distilled under reduced pressure, and **9, 10-dinitro-anthracene** $C_{10}H_8(NO_2)_2$, m.p. 294°. These compounds are easily obtained indirectly. On digesting anthracene in glacial acetic acid with one molecule nitric acid at 30°–35°, we obtain the acetate of **nitro-hydran-**

thranol $CH_2CO_2\rangle C\langle C_6H_4\rangle C\langle NO_2$ / H / C_6H_4 / H, which, with HCl, yields the corresponding chloride, with N_2O_3 the nitrite, and with alcohol the ethers, also produced direct on nitrifying with HNO_3 and the alcohols. On treatment with alkali, the chloride forms 9-nitro-anthracene, and this, treated with NO_2 in chloroform, gives **trinitro-hydranthranol** $(NO_2)_2C\langle C_6H_4\rangle CH(NO_2)$ / C_6H_4, which, with alkali, yields 9, 10-dinitro-anthracene. In a similar manner, **9-ethyl-10-nitro-anthracene** $C_{14}H_{18}(C_2H_5)(NO_2)$, m.p. 135°, has been obtained from ethyl-anthracene. By boiling with alcoholic potash, 9-nitro-anthracene has been transposed, by way of several intermediaries due to the addition of potassium alcoholate, etc., into **anthraquinone-oxime** $CH\langle C_6H_4\rangle C.NO_2 \rightarrow CO\langle C_6H_4\rangle C:NOH$ / C_6H_4 / C_6H_4 (cp. 9-nitro-phenanthrene). When nitric acid acts upon anthracene in iso-butyl alcohol, we obtain **nitro-anthrone** $CO(C_6H_4)_2CH.NO_2$, which is converted by alkali into a red isomer $CO(C_6H_4)_2C:NOOH$ (?) (A. **330**, 133; B. **42**, 1216).

9- or **meso-Amido-anthracene,** *anthramine,* m.p. 145°–150°, from 9-nitro-anthracene with $SnCl_2$ and HCl; dinitro-anthracene cannot be reduced to diamido-anthracene. The 9-anthramine, like the *α*- or **1-anthramine,** m.p. 130°, and the *β*- or **2-anthramine,** m.p. 237°, has also been obtained from the corresponding oxy-anthracenes by heating with NH_3. With diazo-benzol chloride, the 9-amido-anthracene unites to form **benzol-azo-meso-anthramine** $C_6H_5N:N.C_{14}H_8.NH_2$, m.p. 183°, which is split up by acids into anthraquinone, phenyl-hydrazin, and ammonia (B. **40**, 518), and passes on reduction into the easily oxidised **1, 4-anthra-diamine** (B. **41**, 1434); **meso-phenyl-anthramine,** m.p. 203° (C. 1909, II. 1249).

Anthracene-sulphonic acids are formed from anthracene with sulphuric acid, and by reduction of anthraquinone-sulphonic acids. **1-Anthracene-sulphonic acid,** see B. **37**, 70. On moderate treatment with dilute sulphuric acid, anthracene yields **2-anthracene-monosulphonic acid** $C_{14}H_9.SO_2H$, chloride, m.p. 122° (B. **28**, 2258). Concentrated H_2SO_4 produces 1, 5- and 1, 8-anthracene-disulphonic acids (chlorides, m.p. 249° and 225°), which, on fusion with potash, form the corresponding dioxy-anthracenes *rufol* and *chrysazol* (B. **42**, 1413).

Oxy-anthracenes: (1) $C_6H_4\langle CH / CH \rangle C_6H_3OH$. (2) $C_6H_4\langle COH / CH \rangle C_6H_4$.

(1) *α*- and *β*-**Monoxy-anthracene, α- and β-anthrol,** behave like phenols or naphthols. *α*-Anthrol, from 1-anthracene-monosulphonic acid by fusion with potash, forms yellowish flakes, melting at 152° (B. **37**, 71). *β*-Anthrol, from *β*-anthracene-sulphonic acid and *β*-oxy-anthraquinone, is changed by nitrous acid to ***α*-nitroso-*β*-anthrol** $C_6H_4(CH)_2C_6H_2(OH)(NO)$, which, upon reduction, yields ***α*-amido-*β*-anthrol.** The latter may be oxidised to **1, 4-anthraquinone** $C_6H_4\langle CH—C—CO—CH / CH—C—CH—CH \rangle$, melting with decomposition at 208°, and isomeric with *α*-naphtho-quinone (B. **39**, 926; **41**, 1434; A. **344**, 78). 1, 2-Anthraquinone, similarly formed from the *α*-anthrol, gives on reduc-

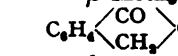
tion with zinc dust and glacial acetic acid **1, 2-anthra-hydroquinone** $C_6H_4(CH)_2C_6H_2(OH)_2$, m.p. 131° with decomposition (A. **342,** 59). The anthrols can only be oxidised by CrO_3 to oxy-anthraquinones after acetylating the OH group (cp. oxidation of phenols). The 1, 2-anthra-hydroquinones in this manner yields alizarin.

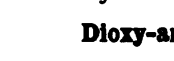
Benzo-dioxy-anthracenes.—Two isomerides—**chrysazol** and **rufol,** m.p. 225° and 265°—having the formula $OH.C_6H_3 : (CH)_2 : C_6H_2OH$, are obtained from α- and β-anthracene-disulphonic acids. When their acetyl derivatives are oxidised and saponified, **chrysazine** and **anthrarufin** result. These are the corresponding dioxy-anthraquinones.

2, 3-Dioxy-anthracene, decomposing at 180° by reduction of hystazarin-dimethyl ether with zinc dust and NH_3, and saponification with HI (A. **342,** 90).

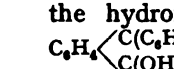
(2) **meso-Oxy-anthracene, anthranol** $C_6H_4\langle\begin{smallmatrix}COH\\CH\end{smallmatrix}\rangle C_6H_4$, yellowish-brown needles, m.p. 120° when quickly heated, desmotropic with **anthrone** $C_6H_4\langle\begin{smallmatrix}CO\\CH_2\end{smallmatrix}\rangle C_6H_4$, colourless brilliant needles, m.p. 155° (A. **379,** 37). The latter is formed synthetically from o-benzyl-benzoic acid $C_6H_4\langle\begin{smallmatrix}CH_2C_6H_5\\COOH\end{smallmatrix}$ with concentrated sulphuric acid at 90° (B. **27,** 2789), also from phthalide chloride, benzene, and $AlCl_3$, and is obtained by reduction of anthraquinone with tin or zinc and glacial acetic acid besides dianthryl $(C_{14}H_9)_2$ (A. **379,** 55 ; C. 1908, II. 1218). Anthranol acetate, m.p. 134°, is also formed by the oxidation of anthracene and PbO_2 in glacial acetic acid (A. **379,** 75). The anthrone is insoluble in cold alkali, but dissolves on heating with formation of salts of anthranol, which can be precipitated from this solution by a careful addition of dilute H_2SO_4. The isomers capable of independent existence in the solid state, form, on solution or melting, an allelotropic mixture of both forms, in which the more stable anthrone is predominant. The solutions therefore show reactions characteristic of both forms : on heating with acetic anhydride we obtain anthranol acetate, but on alkylating with C_2H_5I and potash we obtain, simultaneously, **anthranol-ethyl ether** $CH\langle\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\rangle COC_2H_5$, liquid, **ethyl-anthranol-ethyl ether** $C_2H_5C\langle\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\rangle COC_2H_5$, m.p. 77°, and **diethyl-anthrone** $(C_2H_5)_2C\langle\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\rangle CO$, m.p. 136° (B. **21,** 2505). With benzaldehyde, anthrone condenses, under the influence of piperidin, to **benzylidene-anthrone** $C_6H_5CH : C(C_6H_4)_2CO$, yellow needles, m.p. 127° (C. 1906, I. 138) ; with benzo-phenone chloride to **diphenyl-anthraquinone-methane** $(C_6H_5)_2C : C(C_6H_4)_2CO$, m.p. 196° (C. 1910, I. 1722). With benzol-diazonium chloride it forms **benzol-azo-anthranol** $C_6H_5N : NC\langle\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\rangle COH$, m.p. 183°, identical with the anthraquinone-monophenyl-hydrazone formed from dibromanthrone $CBr_2(C_6H_4)_2CO$, m.p. 157°, and phenyl-hydrazin (B. **40,** 518). By the action of atmospheric oxygen, or mild oxidisers like $FeCl_3$, HgO, etc., anthrone and anthranol are oxidised to **meso-dihydro-dianthrone** $CO(C_6H_4)_2CH.CH(C_6H_4)_2CO$, m.p. 245°, which is also obtained from mono-bromanthrone, m.p. 148°, by heating with copper powder. It is insoluble in alkalies, but, on heating with alcoholic alkali, it forms the alkali

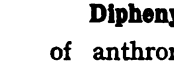
salt of **dianthranol** HOC COH, yellowish crystals, m.p. 230°, easily obtained by reduction of anthraquinone, with zinc dust and soda under pressure at 160°, and transposed by alcoholic HCl into meso-dihydro-dianthrone. By oxidation with $FeCl_3$ it passes into the **dianthrone** $CO(C_6H_4)_2C:C(C_6H_4)_2CO$, analogous to dipheno-quinone, in the shape of a lemon-yellow powder from which zinc dust and glacial acetic acid regenerate dianthranol (M. **30,** 165).

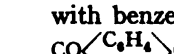
β-Methyl-anthrone, m.p. 87° (C. 1910, I. 1722). **Oxy-anthrone**  , m.p. 221°, is prepared from oxy-dimethyl-methane-o-carboxylic acid (B. **31,** 2793). **Dimethyl-amido-anthrone** $C_{14}H_{10}O[N(CH_3)_2]$, m.p. 80°–85°, is obtained from o-dimethyl-amido-benzyl-benzoic acid, with H_2SO_4 (A. **307,** 313).

Dioxy-anthrone  , so-called **anthrarobin,** results when alizarin is reduced with zinc dust and ammonia. It has been applied therapeutically in certain skin diseases.

A few isomeric dioxy-anthranols have been obtained by reduction of quinizarin, anthra-rufin-hystazarin, and chrysazin with HI (B. **35,** 2923, 2930; **36,** 2938).

meso-Phenyl-anthrone $C_6H_5CH(C_6H_4)_2CO$, m.p. 141°–144°, is formed when sulphuric acid acts upon triphenyl-methane-o-carboxylic acid. Its oxidation product is phenyl-oxanthrone. It yields phenyl-anthracene by reduction. Substituted triphenyl-methane-carboxylic acids form substituted phenyl-anthrones. In accordance with their source, the hydroxyl-phenyl-anthrones, like **dioxy-phenyl-anthrone,**  , have been designated **phthalidins** because they are formed from the phthalins, the reduction products of the phthaleïns or diphenol-phthalides. When oxidised, the phthalidins become *phthalideïns,* hydroxyl-phenyl-oxanthranols.

Diphenyl-anthrone  , m.p. 192°, is a derivative of anthrone. It is obtained by condensing unsym. phthalylene tetrachloride with benzene, as well as from phenyl-oxanthrone by means of benzene and sulphuric acid (B. **28,** R. 772).

On reduction with zinc dust and glacial acetic acid it yields **9, 9-diphenyl-dihydro-anthracene.** Mixed diaryl-anthrones are obtained, either from phenyl-oxanthrone, benzene homologues, and H_2SO_4, or, with benzene derivatives and $AlCl_3$, from **phenyl-oxanthranyl chloride**  , m.p. 164°; the latter is formed from diphenyl-phthalide on heating with PCl_5 to 140° (C. 1898, I. 209; 1899, II. 204). With phenols it condenses on simply heating the components to form oxy-diphenyl-anthrones (B. **88,** 3802). **meso-Dichloranthrone** $CO(C_6H_4)_2CCl_2$, m.p. 133°, from o-tolyl-phenyl-ketone by heating with chlorine to 120°, or by heating anthrone with Cl, gives, with dimethyl-aniline and $AlCl_3$, **tetramethyl-diamido-diphenyl-anthrone** $[(CH_3)_2NC_6H_4]_2C(C_6H_4)_2CO$, yellow needles, m.p. 278° (C. 1903, I. 837).

From anthrone, also, the group of *anthro-cumarins* can be derived. These are produced by condensing cinnamic acids and oxy-benzoic

acids by means of sulphuric acid. **Anthra-cumarin** $\begin{matrix}C_6H_4—C=CH\\ CO—C_6H_3—O\end{matrix}\!\!>\!CO$, m.p. 260°, from m-oxy-benzoic acid and cinnamic acid; **dioxy-anthra-cumarin,** styro-gallol, from gallic and cinnamic acids (B. **20,** 2588, 3143; C. 1899, II. 967). Cp. also the *benzoïn yellow* $\begin{matrix}C_6H_4—C=\!=\!=CC_6H_5\\ CO—C_6H(OH)_2.O\end{matrix}$ (?) produced from benzoïn and gallic acid (B. **31,** 2975).

meso-Dioxy-anthracene, *anthra-hydroquinone* $C_6H_4\!<\!\begin{matrix}C(OH)\\ C(OH)\end{matrix}\!>\!C_6H_4$, brown needles, with a diaceto-compound melting at 260°, desmotropic with **oxanthrone** $C_6H_4\!<\!\begin{matrix}CO——\\ CH(OH)\end{matrix}\!>\!C_6H_4$, white needles with a yellow tinge, m.p. 167°, are related to each other like anthranol and anthrone, except that mutual transformation in solutions is exceedingly slow, and that the enol-form, anthra-hydroquinone, is the more stable. Anthra-hydroquinone is formed by reducing anthraquinone with zinc dust and potash; it oxidises back to anthraquinone in the air. In alkalies it easily dissolves with a red colour. Treatment with alcoholic HCl converts it, to a slight extent, into oxanthrone, which is easily obtained by heating bromanthrone with aqueous acetone, or direct, by the action of bromine upon anthracene in aqueous acetone solution. Reduction with zinc dust and glacial acetic acid produces anthranol and anthrone respectively. Heating with alkali or alcoholic HCl converts oxanthrone into anthro-hydroquinone. On alkylating anthra-hydroquinone with alkyl iodide or dialkyl sulphate and alkali, the mono- and dialkyl ether of anthra-hydroquinone and alkyl-oxanthrone are obtained together $C_6H_4\!<\!\begin{matrix}CO\\ C(OH)Alk\end{matrix}\!>\!C_6H_4$ (A. **379,** 43).

Anthracene-carboxylic Acids.—The α- and β-acids $C_6H_4(CH)_2C_6H_3COOH$ are formed from the anthracene-monosulphonic acids by means of the cyanides, and from the anthraquinone-carboxylic acids by reduction with ammonia and zinc dust; the α-acid melts at 245°, the β-acid at 281°.

meso-Anthracene-carboxylic acid is formed from its chloride, which is produced when anthracene is heated with phosgene or, better, oxalyl chloride, to 160° (B. **44,** 205). It melts at 217° with decomposition. Chromic acid oxidises it to anthraquinone.

meso-Benzoyl-anthracene, *anthra-phenone* $C_{14}H_9.COC_6H_5$, m.p. 148°, is obtained from anthracene, benzoyl chloride, and zinc dust or $AlCl_3$. In the latter case two isomers, melting at 75° and 203° respectively, are also obtained (B. **33,** 816; **34,** 2766).

Hydro-anthracenes.—**Anthracene dihydride** $C_{14}H_{12}$ results from the action of sodium amalgam upon the alcoholic solution of anthracene. It can also be obtained by many other synthetic methods. On heating with hydriodic acid or with hydrogen and nickel at 200°–250°, we obtain **tetra-, -hexa-, -octo-,** and **-perhydride** $C_{14}H_{14}$, $C_{14}H_{16}$, $C_{14}H_{18}$, and $C_{14}H_{24}$, m.p. 89°, 63°, 71°, and 88°, b.p. 310°, 290°, 293°, and 270° (B. **21,** 2510; **41,** 996; *A. Chim. Phys.* 8, **12,** 468).

meso-Alkylic derivatives of anthracene dihydride are produced in the reduction of the alkyl-oxanthrones, and meso-dialkyl derivatives synthetically from alkylidene chlorides, benzene, and $AlCl_3$.

meso-Dimethyl-anthracene hydride $C_6H_4(CH.CH_3)_2C_6H_4$, m.p. 181°, yields anthraquinone by oxidation (A. **235,** 305), just as benzo-phenone

is obtained from unsym. diphenyl-ethane. It is obtained from ethylidene chloride, benzene, and $AlCl_3$. meso-Diphenyl-anthracene hydride, m.p. 153°, from benzal chloride, benzene, and $AlCl_3$, besides triphenylmethane (*Am. Ch. J.* **18,** 556).

9, 9-Diphenyl-dihydro-anthracene $(C_6H_5)_2C(C_6H_4)_2CH_2$, m.p. 196°, by reduction of diphenyl-anthrone with zinc dust in glacial acetic acid (B. **38,** 1800).

Anthraquinone or diketo-dihydro-anthracene must be included with the derivatives of dihydro-anthracene. Thereto belong also:

Anthrone and **oxanthrone,** which have already been discussed in connection with anthranol and dioxy-anthraquinone. We must also include **dihydro-anthranol** $C_6H_4\langle\begin{matrix}CH(OH)\\CH_2\end{matrix}\rangle C_6H_4$, m.p. 76°, obtained by reducing anthraquinone with zinc dust and ammonia. It easily decomposes into water and anthracene on standing in air. The alkyl derivatives of dihydro-anthranol $C_6H_4\langle\begin{matrix}CR(OH)\\CH_2\end{matrix}\rangle C_6H_4$ are obtained by reduction of the alkyl-oxanthrones, or, direct, by the reduction of anthraquinone with zinc dust and soda in the presence of halogen-alkyls. Like dihydro-anthranol, they easily split off water on boiling with HCl and pass into γ-alkyl-anthracenes (B. **18,** 2150; **24,** R. 768; A. **212,** 67).

meso-Triphenyl-hydranthranol $(C_6H_5)_2C(C_6H_4)_2C(OH)C_6H_5$, m.p. 200°, from diphenyl-anthrone with C_6H_5MgBr, gives on reduction **triphenyl-hydranthracene** $(C_6H_5)_2C(C_6H_4)_2CHC_6H_5$, m.p. 220°. The latter also results from the condensation product of triphenyl-methane-carboxylic ester with C_6H_5MgBr by treatment with H_2SO_4 (C. 1904, II. 530).

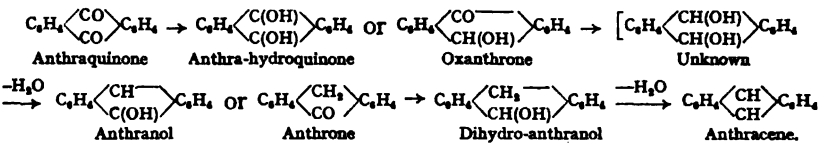
Phenyl-oxanthrone is formed by the oxidation of phenyl-anthrone, and the action of C_6H_5MgBr upon anthraquinone. In a similar manner, several further meso-aryl- and meso-alkyl-anthracenes have been converted into the corresponding oxanthranones. Thus we get the **tetramethyl-diamido-phenyl-oxanthrone** $(CH_3)_2NC_6H_4\rangle C(HO)\langle\begin{matrix}C_6H_4\\C_6H_3N(CH_3)_2\end{matrix}\rangle CO$, m.p. 213°, from the condensation product of tetramethyl-diamido-diphenyl-methane-o-carboxylic acid. It combines with dimethyl-aniline and $POCl_3$ to form the dyestuff Phal green, the chloride of the base $C_6H_4\langle\begin{matrix}C(OH)[C_6H_4N(CH_3)_2]\\C(OH)[C_6H_4N(CH_3)_2]\end{matrix}\rangle C_6H_3N(CH_3)_2$ (C. 1903, II. 1180), which is based upon **diphenyl-dioxy-anthracene hydride** $C_6H_4[C(OH)C_6H_5]_2C_6H_4$, m.p. 242°. The latter, from anthraquinone with phenyl-magnesium bromide, condenses easily, like meso-triphenyl-hydranthranol, with phenols and aromatic amines to tetra-aryl-dihydro-anthracenes (C. 1904, I. 814; 1905, I. 744).

Dimethyl- and **diethyl-dioxy-anthracene hydride** $C_6H_4[CR(OH)]_2C_6H_4$, m.p. 181° and 175°, from anthraquinone, with methyl- and ethyl-magnesium iodide respectively (C. 1906, I. 47).

Anthraquinone, *diphenylene-diketone* $C_6H_4(CO)_2C_6H_4$, melting at 285° and boiling at 382°, sublimes in yellow needles. It is not only produced by synthetic methods, but also quite easily by the oxidation of anthracene with a chromic acid mixture (technical preparation, A. Suppl. **7,** 285), as well as from anthra-hydride, meso-dichloro-, dibromo-, and dinitro-anthracene. It is, compared with the isomeric phenanthra-

quinone, very stable toward oxidants. It combines with hydroxylamine to anthraquinone-oxime, subliming above 200°. Sulphurous acid does not reduce it (unlike the true quinones).

It reverts to anthracene if heated to 150° with hydriodic acid, or with zinc dust and ammonia. A variety of intermediate products are obtained in this reaction by simply applying different reducing agents :



On digesting with zinc dust and soda, anthra-hydroquinone is formed, and its red alkaline solution, shaken in air, regenerates anthraquinone (qualitative test for anthraquinone).

When fused with potassium hydroxide (at 250°), it decomposes into two molecules of benzoic acid ; heated with soda-lime, it yields benzene and a little diphenyl.

Homologous anthraquinones are obtained partly in the synthetic way and in part by the oxidation of benz-alkylic anthracenes.

Methyl-anthraquinone $C_6H_4(CO)_2C_6H_3.CH_3$, melting at 177°, from nitric acid and methyl-anthracene, is also present in crude anthraquinone.

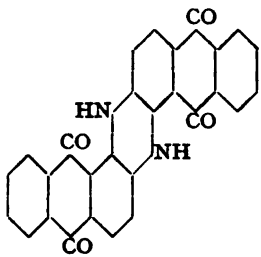
Substituted Anthraquinones.—Halogen-anthraquinones are formed (1) by the action of chlorine or bromine upon anthraquinone ; (2) from chlorine- and bromine-anthracenes by oxidation ; (3) from amido-anthraquinones by means of their diazonium salts (B. **37,** 59) ; (4) by the action of chlorine and bromine upon anthraquinone or anthracene-sulphonic acids in aqueous solution, the sulpho-groups being easily replaced by halogen (C. 1909, I. 414 ; 1911, I. 102) ; (5) by synthesis from halogen-benzo-phenone-o-carboxylic acids : **1-chloro-, bromo-,** and **iodo-anthraquinone,** m.p. 209°, 205°, and 176° ; from **2-bromo-anthraquinone** and from **dibromo-anthraquinone,** alizarin is obtained by fusing with potash. The halogen atoms in the α-position can easily be replaced by the groups OH, OR, OC_6H_5, NH_2, and NHR on heating with lime-water, sodium alcoholate or phenolate, ammonia or amines, if necessary with an addition of copper salts.

Nitro-anthraquinones.—From anthracene or anthraquinone, by heating with nitric acid, we obtain besides **1-nitro-anthraquinone,** m.p. 230°, chiefly **1, 5-dinitro-anthraquinone** (C. 1906, I. 1070). **2-Nitro-anthraquinone,** m.p. 185°, has been obtained from 2-amido-anthraquinone by transposition of the diazonium salt with sodium-copper nitrite ; also from 3-amido-2-nitro-anthraquinone, by eliminating the amido-group ; and synthetically from o-benzoyl-p-nitro-benzoic acid (B. **37,** 4435 ; **38,** 295). By moderate alkaline reduction of the nitro-anthraquinones we obtain comparatively stable **β-hydroxyl-amino-anthraquinones** $C_{14}H_7O_2(NHOH)$, $C_{14}H_6O_2(NHOH)_2$, which, by transposition with acids, yield amino-oxy-anthraquinones (B. **35,** 666).

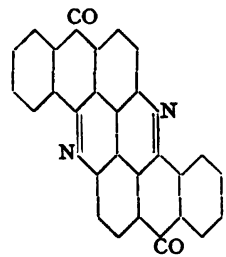
Amido-anthraquinones and their derivatives have lately acquired great technical importance, since some of them, like the benzoyl-amido-anthraquinones and tri-anthraquinone-di-imides, have the character

of vat dyes, and some of them, like 2-amido-anthraquinone, can be easily converted into these by simple operations. Vat dyes are dyes insoluble in water and alkalies, which can be converted by alkaline reduction into hydro-compounds soluble in alkali, and then have the faculty of combining with the fibre, and of regenerating the original dye on the fibre by subsequent oxidation in air. All vat dyes contain one or more CO groups, and their character depends upon the possibility of converting these groups into OH groups capable of forming salts. The vat dyes are mostly distinguished by their great permanence (B. **48,** 987; *Ch. Ztg.* **34,** 731).

Amino-anthraquinones are formed (1) by the reduction of nitro-anthraquinones; (2) synthetically from amino-benzoyl-o-benzoic acid by condensation (C. 1909, I. 475); (3) by replacing nitro-, halogen-, sulpho-, and hydroxyl-groups in the α- or 1-position in anthraquinone by NH_2 or NHR groups, on heating with ammonia, amines, and particularly anilines, with the possible addition of copper powder (C. 1901, II. 1379; 1902, II. 368, etc.). **1- and 2-Amino-anthraquinone,** red needles, m.p. 242° and 302°. The 2-amino-anthraquinone is converted, by fusion with potash at 250°, into the interesting and valuable vat dye *indanthrene* (*q.v.*), and under different conditions, such as heating with aluminium chloride or, better, by boiling with antimony pentachloride in nitro-benzene solution, into the similar but yellow-coloured *flavanthrene* (*q.v.*):



Indanthrene



Flavanthrene.

Di- and poly-amido-anthraquinones have been obtained by the reduction of poly-nitro- or nitro-amido-anthraquinones, usually with sodium sulphide: **1, 4-, 1, 5-,** and **1, 8-diamido-anthraquinones** melt at 268°, 319°, and 262° (C. 1902, II. 1232; B. **88,** 637). 1, 2- and 2, 3-Diamido-anthraquinones condense like o-phenylene-diamines with o-diketones to azins (B. **37,** 4531; C. 1906, II. 80).

As already mentioned, numerous acyl-derivatives of amido-anthraquinones, especially benzoyl-amido-anthraquinones, are directly useful as vat dyes. The latter are either obtained from amido-anthraquinones with benzoyl chloride or from halogen-anthraquinones with benzamide and copper powder. Benzoyl-α-amido-anthraquinone and dibenzoyl-1, 5- and 1, 8-diamido-anthraquinone give yellow colorations, which are slightly displaced towards red by the substitution. The amido-anthraquinone derivatives of dicarboxylic acid, malonic acid, succinic acid, phthalic acid, etc., possess to some extent the character of vat dyes. To these belong the dyes known as algol-yellow W.G., algol-pink R, and algol-scarlet G.

Dianthra-quinonimides, *dianthrimides*

$$C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4.NH.C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle C_6H_4,$$

and **trianthraquinone-di-imides,** *trianthrimides* **A**—NH—**A**—NH—**A** are formed by the condensation of mono- and diamido-anthraquinones with halogen-anthraquinones by boiling the components with sodium acetate in nitro-benzol with perhaps some copper powder (C. 1905, II. 1206). They possess an immediate dyestuff character, though some of them require further transformations to produce vat dyes. Some of their names are: indanthrene-claret B, indanthrene-red G, algol-orange R, algol-claret 3B, and algol-red B.

Like o-amido-benzaldehyde and o-amido-acetophenone, α-amido-anthraquinone is capable of forming heterocyclic ring-systems, the linkage being in the 1, 9-position with respect to the anthraquinone nucleus. Thus, by condensation with acetone and soda, analogous to the formation of quinaldin from o-amido-benzaldehyde, we obtain a *c-methyl-anthra-pyridin* $\begin{matrix}C_6H_4.C:CH.C.CH_3\\CO—C_6H_3\,.\,N\end{matrix}$ (C. 1907, II. 863). With methane, α-amido-anthraquinone combines to form *anthra-pyrimidone* $\begin{matrix}C_6H_4.C:N.CO\\CO—C_6H_3.NH\end{matrix}$ (C. 1909, I. 327), with formamide to *anthra-pyrimidin* $\begin{matrix}C_6H_4.C:N.CH\\CO—C_6H_3.N\end{matrix}$ (C. 1910, I. 1305). Other hetero-ring formations, see C. 1902, II. 368; 1906, II. 386; 1908, II. 1658.

The action of NO_3H upon the free amido-anthraquinones leads to the very stable nitro-nitramino-anthraquinones (B. **37,** 4227). The simplest **1-nitramino-anthraquinone** $C_{14}H_7O_2.NHNO_2$, yellow needles, m.p. 193° with decomposition, is formed by the oxidation of 1-anthraquinone-diazonium sulphate with sodium hypochlorite (C. 1905, I. 313). Somewhat easier is the nitrification of the acetyl compounds and the urethanes of the amido-anthraquinones, the former yielding chiefly p-nitro-, and the latter o-nitro- and o, p-dinitro-amido-anthraquinones (C. 1906, II. 468).

On bromination 1-amido-anthraquinone gives **2-bromo-** and **2, 4-dibromo-anthraquinone,** m.p. 181° and 222°, whereas 2-amido-anthraquinone gives the **1, 3-dibromo-2-amido-anthraquinone** (B. **40,** 1701; C. 1905, I. 1447). The 2-bromo-compound is of especial interest, since, by heating with sodium acetate in nitro-benzol solution and addition of copper chloride, it can be transformed into indanthrene (C. 1905, I. 843).

Anthraquinone-sulphonic Acids.—Heating anthraquinone with fuming sulphuric acid produces a little 1-anthraquinone-sulphonic acid, but chiefly 2-anthraquinone-sulphonic acid, and on further sulphuration 2, 6- and 2, 7-acids are formed. On adding some finely divided mercury salt to this sulphurated mixture, the 1-acid is mostly produced, with some 1, 5- and 1, 8-acid. 1-Monosulphonic acid, sulphurated with mercury salt, yields 1, 6- and 1, 7-disulphonic acid. Sulpho-groups in the 1-position, on being heated with NH_3, or amines, are easily replaced by NH_2 or NHR groups; with methyl-alcoholic potash or potassium phenolate they are replaced by CH_3O or C_6H_5O groups; and on heating with lime-water under pressure by HO groups (B. **36,** 4194; **37,** 66, 331, 646). On fusing with potash these acids, which contain the

sulpho-groups in the 2-position, yield both normal and higher hydroxylated products :

2-Anthraquinone-monosulphonic acid —{→ 2-Oxy-anthraquinone; → Alizarin (1, 2 OH)

2, 6-Anthraquinone-disulphonic acid —{→ Anthra-flavinic acid (2, 6 OH); → Flavo-purpurin (1, 2, 6 OH)

2, 7-Anthraquinone-disulphonic acid —{→ Iso-anthra-flavinic acid (2, 7 OH); → Anthra-purpurin (1, 2, 7 OH) etc.

The sulpho-acids of the amido-alkyl-amido- and aryl-amido-anthraquinones are to a great extent valuable wool-dyes, *e.g.* **alizarin saphirol** $NH_2[8]SO_3H[6]OH[5]C_6H\langle{}^{CO}_{CO}\rangle C_6H[1]OH[2]SO_3H[4]NH_2$, obtained by reduction of dinitro-anthrarufin-disulphonic acid ; ***alizarin pure blue*** $C_6H_4\langle{}^{CO}_{CO}\rangle C_6H[1]NH_2[2]Br[4]NHC_7H_6SO_3H$, alizarin-cyanin green, anthraquinone green, and many others. They are formed mostly by transformation of α-halogen, or α-nitro- or α-oxy-anthraquinones, with ammonia, or aliphatic or aromatic amines, and subsequent sulphuration (B. **34,** 2344 ; C. 1904, II. 339).

A summary of the literature of the anthraquinone-sulphonic acids and their derivatives is found in *Chemische Industrie,* **32,** 477.

The **oxy-anthraquinones** are derived (1) from the bromo- and chloro-anthraquinones and from the sulphonic acids on fusion with alkalies, when the substituting groups are replaced by hydroxyls.

By stronger fusion there generally ensues an additional entrance of hydroxyl (oxy- and dioxy-anthraquinones result from the mono-sulphonic acids) ; the same is true in the fusion of the oxy-anthraquinones (B. **11,** 1613).

(2) The oxy-anthraquinones may be synthetically prepared on heating phthalic anhydride with phenols (mono- and poly-valent) and sulphuric acid to 150°. The m-oxy-benzoic acids and oxy-benzoyl-o-benzoic acids also yield them when similarly treated (C. 1908, I. 1697).

The introduction of hydroxyl into anthraquinone and the oxy-anthraquinones can be effected practically by persulphates in sulphuric acid solution. One or several hydroxyl groups will then enter the anthraquinone molecule, depending upon the conditions which prevail (B. **29,** R. 988).

Continued fusion with alkalies causes the oxy-anthraquinones to separate into their component oxy-benzoic acids (in the same way as anthraquinone decomposes into benzoic acid), and this reaction aids in the determination of the position of the isomerides (B. **12,** 1293 ; A. **280,** 1).

Oxy-anthraquinones are reduced to anthracene when heated with zinc dust.

Individual hydroxyls in the oxy-anthraquinones are reduced by heating the latter with stannous chloride and sodium hydroxide (A. **183,** 216). Heated to 150°–200° with ammonia water, single OH groups are replaced by amide groups.

During the etherification of the oxy-anthraquinones a striking rule is observed, recalling the etherification of the benzoic acids. Only the hydroxyls in the β-position, but not those in the α-position, are etherified on treatment with halogen alkyls or dialkyl sulphate and alkali. This behaviour has been used successfully for determinations of constitution.

The oxy-anthrones and oxy-anthracenes show no such impediment to reaction (A. **349**, 201).

(*a*) *Monoxy-anthraquinones* $C_{14}H_7O_2(OH)$ the α- or **erythro-oxy-anthraquinone,** melting at 190°, and the β- at 323°, are formed simultaneously on heating together phenol and phthalic anhydride. The β-body is also prepared from β-bromo- or sulpho-anthraquinone.

Both oxy-anthraquinones yield *alizarin* when fused with caustic potash.

(*b*) *Dioxy-anthraquinones.*—The members of this group containing two OH groups in the 1, 2-position are especially interesting, because they unite with metallic oxides to form insoluble, very stable *lakes*, which adhere closely to the fibre. Their colour varies with the character of the metal. They are, therefore, very valuable mordant dyes (B. **21**, 435, 1164) (compare the similar behaviour of the dioxy-benzophenones, and *naphthazarin*, etc. For the theoretical side, consult B. **26**, 1574). Alizarin, 1, 2-dioxy-anthraquinone, is the most important of these dyes.

Nine of the ten possible isomeric dioxy-anthraquinones are known.

Alizarin, 1, 2-*dioxy-anthraquinone*, melting at 290° and subliming at higher temperatures in orange-red needles, is the chief constituent of the dye of the madder root (*Rubia tinctorium*), in which it is contained as *ruberythric acid* (identical with morindin, from *Morinda citrifolia*).

Through the action of a ferment in the madder root, or when it is boiled with dilute acids or alkalies, ruberythric acid decomposes into glucose and alizarin :

Ruberythric acid $C_{26}H_{28}O_{14}+2H_2O=2C_6H_{12}O_6+C_{14}H_6O_2(OH)_2$ Alizarin.

The alizarin products (*garancin*, etc.) obtained by such decompositions of madder root were formerly used in dyeing. At present they have been almost entirely supplanted by pure synthetic alizarin.

Artificial alizarin was first obtained by Graebe and Liebermann, in 1868, by heating dibromo-anthraquinone with potassium hydroxide. They had previously observed that the natural alizarin yielded anthracene when it was heated with zinc dust. Alizarin is also produced from dichloro- and monobromo-anthraquinone, from the two oxy-anthraquinones and anthraquinone-sulphonic acid, by fusion with caustic potash.

Technically, it is made from anthraquinone prepared from purified (50 per cent.) anthracene. The latter is converted by fuming sulphuric acid into anthraquinone-monosulphonic acid, which is then fused under pressure for several days with caustic soda at a temperature ranging from 180°–200°. Potassium chlorate is added as an oxidising agent. The product of the reaction is sodium-alizarin, which is then decomposed with hydrochloric acid and brought into the market in the form of a paste (10–20 per cent.).

Alizarin also results, together with isomeric hystazarin, on heating phthalic anhydride with pyro-catechin and sulphuric acid.

Alizarin dissolves readily in alcohol and ether, and sparingly in hot water. It dissolves with a purple-red colour in the alkalies ; lime and barium salts throw out the corresponding salts as *blue* precipitates. Alums and tin salts produce *red-coloured* precipitates (madder lakes) ; while ferric salts form *blackish-violet*, and chromium salts *violet-brown* precipitates.

In cotton dyeing and printing the beautiful red lake and the almost black iron lake are generally employed. The goods are mordanted with alumina (by immersing them in aluminium acetate and then heating, whereby aluminium hydroxide is deposited on the fibres) and then dipped into the solution of alizarin; the resulting alizarin aluminate is fixed by the fibres. In dyeing with turkey-red it is customary to mordant the cloth with oil and alum, when the alumina then unites both with the oleic acid and with the alizarin.

Alizarin is decomposed by protracted fusion with caustic potash into benzoic and proto-catechuic acids.

Alizarin-dimethyl ether $C_{14}H_6O_2(OCH_3)_2$, m.p. 215°, results from 1, 2-dimethoxy-anthrone on oxidation, and from 1-nitro-2-methoxy-anthraquinone by heating with methyl-alcoholic potash. On saponification with concentrated H_2SO_4 it yields the **alizarin-2-monomethyl ether,** m.p. 230°, also obtained by direct methylation of alizarin (A. **349,** 201). The isomeric **alizarin-1-monomethyl ether,** m.p. 179°, hitherto unobtainable by synthesis, is found, besides hystazarin-monomethyl ether and anthragallol-1, 2-, and -1, 3-dimethyl ether, in the root of *Oldenlandia umbellata* ("chaz root") (C. 1908, I. 646).

β-Nitro-alizarin, *alizarin orange* $C_6H_4(CO)_2C_6H(OH)_2(3)NO_2$, consists of orange-red leaflets, melting at 244°. It is produced by nitrating alizarin in glacial acetic acid or by the action of NO_2 vapours. It is prepared technically. Its alumina lake is *orange* in colour.

The **β-amido-alizarin** obtained by the reduction of β-amido-alizarin forms with acetic anhydride an anhydro-base, and therefore contains the NH_2 group in the o-position with respect to an OH group (B. **18,** 1666; **35,** 906).

Alizarin blue, a derivative of anthraquinolin (B. **18,** 447), results upon heating it with glycerol and sulphuric acid. (See Skraup's quinolin synthesis) (B. **18,** 447). The isomeric **α-nitro-alizarin** $C_6H_4(CO)_2C_6H(OH)_2[4]NO_2$, m.p. 195°, is formed by nitrifying diacetyl-alizarin (cp. B. **24,** 1610). The α-amido-alizarin obtained by reduction gives, with glycerin, nitro-benzol, and sulphuric acid, a green dye, *alizarin green*, isomeric with alizarin blue.

1-Oxy-2-amido-anthraquinone, alizarin amide $C_{14}H_6O_2(OH)NH_2$, m.p. 225°, is obtained by heating alizarin with ammonia water to 200° (B. **39,** 1201).

Amido-oxy-anthraquinones can also be prepared from the hydroxyl-amido-anthraquinones obtained by the reduction of nitro-anthraquinones, by transposing them with sulphuric acid (B. **29,** 2934; **35,** 666); also by the action of fuming sulphuric acid upon amino- and alkyl-amino-anthraquinones (C. 1904, II. 1013). **Bromo-alizarin,** see B. **33,** 1664. **Alizarin-sulphonic acid,** see C. 1909, II. 244.

Three of the dioxy-anthraquinones isomeric with alizarin contain the OH groups in one benzene nucleus. They are:

(1, 3)-Purpuro-xanthin, from phthalic anhydride and resorcinol; **(1, 4)-quinizarin,** from hydroquinone; and **(2, 3)-hystazarin**, from pyro-catechin (B. **28,** 116). They are prepared more advantageously from their *ethers*, which result by the condensation of the corresponding dioxy-benzene ethers with phthalic anhydride and Al_2Cl_6 (A. **342,** 99). Quinizarin is also formed in the action of concentrated sulphuric acid and nitrous acid upon anthraquinone and 1-oxy-anthraquinone, a

process in which the sulphate of 1-oxy-4-diazo-anthraquinone could be isolated, which, on further heating with sulphuric acid, splits up into quinizarin and nitrogen (C. 1905, II. 184). On prolonged heating with concentrated H_2SO_4, hystazarin is partly transposed into alizarin (B. **35,** 1778). For derivatives of hystazarin, see B. **30,** 2936.

The following dioxy-anthraquinones containing their OH groups in *different* benzene nuclei (hetero-nuclear) have been mostly obtained from the corresponding disulpho-acids by heating with lime-water :—

1, 5-Anthrarufin, 1, 6- and **1, 7-dioxy-anthraquinone, 1, 8-chrysazin, 2, 6-anthraflavic acid. Iso-anthraflavic acid** is obtained from β-anthraquinone-sulphonic acid. **Chrysazin** is another isomeride. It is obtained from its tetranitro-compound $C_{14}H_2(NO_2)_4(O_2)(OH)_2$, the so-called **chrysammic acid,** by reduction and the replacement of the amido-groups. This latter acid is obtained when aloes are digested with concentrated nitric acid. Consult B. **19,** 2327, upon the spectra of the dioxy-anthraquinones.

Homologous Dioxy-anthraquinones. — **Dioxy-methyl-anthraquinone** $C_{14}H_5(CH_3)O_2(OH)_2$, is **chrysophanic** or **rheinic acid**, melting at 178° (A. **284,** 193). It exists in senna leaves (of the *Cassia* varieties) and in the root of rhubarb (from the *Rheum* variety), together with methyl-chrysophanic acid (A. **309,** 32). Zinc dust reduces it to methyl-anthracene.

Chrysarobin $C_{30}H_{36}O_7$, a reduction product of chrysophanic acid, occurs in goa- and arroroba-powder, a secretion of coloured Brazilian woods. Air oxidises its alkaline solution to chrysophanic acid. The same occurs in the animal organism (B. **21,** 447).

Methyl-alizarin, melting at 250°–252°, is isomeric with dioxy-methyl-anthraquinone. It is obtained from methyl-anthraquinone-sulphonic acid. It is very similar to alizarin.

Various **methyl-purpuro-xanthins** have been prepared by the condensation of 1, 3, 5-dioxy-benzoic acid with o- and m-toluic acids (B. **29,** R. 141).

By the condensation of 5-methyl-phthalic acid with pyro-catechin, besides a **methyl-alizarin,** m.p. 216°, a **methyl-hystazarin** $(OH)_2[6, 7]C_6H_2(CO)_2C_6H_2[2]CH_3$, has been obtained (B. **33,** 1629).

Dimethyl-anthrarufin $(CH_3)(OH)C_6H_2(CO)_2C_6H_2(CH_3)(OH)$ can also be obtained by the action of sulphuric acid upon sym. oxy-toluic acid (B. **22,** 3273).

(*c*) *Trioxy-anthraquinones.*—These are produced on oxidising anthraquinone-disulphonic acids and dioxy-anthraquinones, or by fusing them with alkalies.

Purpurin $C_6H_4\langle{}^{CO}_{CO}\rangle C_6H[1, 2, 4](OH)_3 + H_2O$, melting at 253° (anhydrous) and sublimable, is present with alizarin in the madder root. It is prepared artificially by heating alizarin and quinizarin with manganese dioxide and sulphuric acid to 150°. It is also obtained from tribromo-anthraquinone. It dissolves with a pure red colour in hot water, alcohol, ether, and the alkalies. Lime and baryta water yield purple red precipitates. It yields a beautiful scarlet red with alumina mordants.

Purpurin-amide $C_{14}H_5O_2(OH)_2NH_2$ is obtained on digesting purpurin with aqueous ammonia at 150°.

The following are isomerides of purpurin : **anthragallol** (1, 2, 3), a constituent of *alizarin brown*, **anthra-** or **iso-purpurin** (1, 2, 7), and **flavo-purpurin** (1, 2, 6), applied technically in dyeing and printing, and also **oxy-chrysazin** (1, 2, 5 ?), **oxy-anthrarufin** (1, 2, 5) (A. **349,** 215) and **1, 4, 8-trioxy-anthraquinone** (C. 1905, II. 1142). Consult A. **280,** 1, for the determination of the constitution of these bodies from the decompositions of the disulphonic acids genetically connected with them.

Homologous Trioxy-anthraquinones.—Emodin, and a **trioxy-methyl-anthraquinone,** melting at 203° and isomeric with it, are formed, together with rhamnose, by the decomposition of *frangulin*, from the bark of *Rhamnus frangula*, by means of alcoholic hydrochloric acid (B. **25,** R. 371). Emodin also results from the decomposition of *polygonine.*

An isomeric emodin is aloe emodin, m.p. 224°, which is found in company with *barbaloïn* in many aloe species (C. 1898, II. 211) as well as in senna leaves (C. 1900, II. 871). On oxidation with chromic acid it passes into a dioxy-anthraquinone-carboxylic acid, the so-called *rhein*, which has also been extracted from Chinese rhubarb (C. 1909, II. 622). A trioxy-methyl-anthraquinone isomeric with emodin is probably the **morindone,** m.p. 272°, obtained by splitting up morindin, a glycoside from *Morinda citrifolia.*

(*d*) *Tetra- and Poly-oxy-anthraquinones.*—When oxy-anthraquinones are heated with fuming sulphuric acid, new hydroxyls enter these bodies, para-hydrogen atoms of the non-substituted nucleus being replaced (*J. pr. Ch.* 2, **48,** 231 ; **44,** 103). Thus alizarin yields **quinalizarin**, *alizarin-bordeaux* $C_{14}H_4O_2$-1, 2, 5, 8- $(OH)_4$.

Two tetraoxy-anthraquinones, **anthra-chrysone** and **rufiopin,** are obtained by heating symmetrical dioxy-benzoic acid and opianic acid or proto-catechuic acid with sulphuric acid.

Rufigallic acid is a hexaoxy-anthraquinone $C_{14}H_2O_2$-1, 2, 3, 5, 6, 7- $(OH)_6$, which is formed when gallic acid is heated with sulphuric acid. It dissolves with an indigo-blue colour in alkalies.

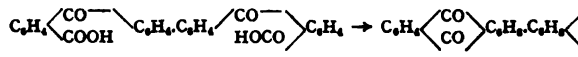
It dyes chrome-mordanted material brown. It appears in trade in conjunction with anthra-purpurin as *alizarin* or *anthracene brown*. *Anthracene blue*, formed by the action of fuming sulphuric acid upon di-nitro-anthraquinone, is an isomeric hexaoxy-anthraquinone.

Anthraquinone-carboxylic acids.—α- and β-**Anthraquinone-carboxylic acids** are produced in the oxidation of anthracene-carboxylic acids. The α-acid (m.p. 285°) is also formed in the condensation of benzoyl-phthalic acid and iso-phthalic acid (B. **29,** R. 284), and the β-acid when chromic acid acts upon methyl-anthracene. The amide of the α-acid, treated with bromine and alkali, yields 1-amido-anthraquinone (B. **30,** 1115). **Trioxy-anthraquinone-carboxylic acid,** *purpurin-carboxylic acid* $C_{14}H_4O_2(OH)_3CO_2H$, is **pseudo-purpurin,** which occurs in crude purpurin (from madder). On heating it decomposes into carbon dioxide and purpurin.

See C. 1894, II. 784, for the synthetic purpurin-carboxylic acids.

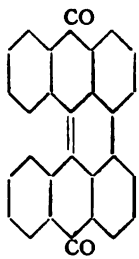
Dianthraquinoyls.—This term is used to designate those compounds in which two anthraquinone residues are directly joined in the α- or β-position. They are formed either on the analogy of diphenyl (1) from the iodo-anthraquinones by heating with powdered copper ; (2) from anthraquinone-diazonium sulphates with acetic anhydride and powdered

copper (B. **40**, 1697; C. 1909, II. 1906); or (3) on the analogy of anthraquinone synthesis by dehydrating the diphenyl-diphthaloyl acids, obtained by heating diphenyl and phthalic anhydride in the presence of $AlCl_3$ (B. **44**, 1075):

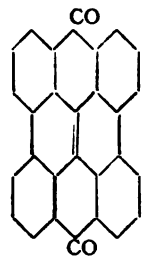


1, 1'-Dianthraquinoyl, yellowish-brown needles, by methods 1 and 2; **2, 2'-dianthraquinoyl,** m.p. 388°, by 1, 2, and 3; **2, 2'-dimethyl-1, 1'-dianthraquinoyl,** m.p. 367°; **2, 4, 2' 4'-tetramethyl-1, 1'-dianthraquinoyl,** m.p. 297° (B. **43**, 512).

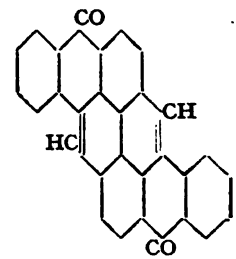
The dianthraquinoyls are distinguished by the fact that they can be easily converted by a further fusion of the anthraquinone nuclei into quinonoid compounds with highly condensed ring systems. Thus the 1, 1-dianthraquinoyl, reduced with Cu or Ni powder and concentrated H_2SO_4, yields **meso-benzo-dianthrone** (similar to meso-dianthrone), steel-blue aggregates resembling hæmatite, and passing on heating with $AlCl_3$ to 140°–145° into **meso-naphtho-dianthrone** (see below), blue needles, with rejection of 2H and further linking of two benzene nuclei (B. **43**, 1734). The 2, 2'-dimethyl-1, 1'-dianthraquinoyl condenses, on heating alone, to 350°–380°, or, better, by boiling with concentrated alcoholic potash and rejection of $2H_2O$ to **pyranthrone,** reddish-brown needles, which resembles flavanthrene in its structure and is related to it, as is anthraflavone to indanthrene (B. **43**, 346):



Meso-benzo-dianthrone



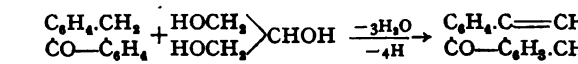
Meso-naphtho-dianthrone



Pyranthrone.

The three compounds all possess the character of vat dyes. Pyranthrone more particularly is known as a specially permanent orange dye under the name of "indanthrene gold-orange."

Benzanthrones.—On heating anthraquinone or, better, anthrone with glycerin and concentrated sulphuric acid to 100°–110°, we obtain the so-called *benzanthrone* with attachment of a new benzene ring in the 1, 9-position (B. **88**, 170):



From the amido-anthraquinone we obtain, with simultaneous formation of a ring containing nitrogen, benzanthrone-quinolins.

Benzanthrone (formula above), light-yellow needles, m.p. 170°; **2-methyl-** and **2, 4-dimethyl-benzanthrone,** m.p. 199° and 165°.

On fusing with caustic potash the benzanthrones, except the oxy-, nitro-, and amido-benzanthrones, close up two molecules and form ex-

cellent vat dyes with a structure resembling pyranthrone and of a blue or violet colour. They are called *violanthrenes* and *iso-violanthrenes*. To these belong *indanthrene dark blue*, and its isomers and substitution products *indanthrene violet* and *indanthrene green*.

Naphthanthracene $C_6H_4\langle{}^{CH}_{CH}\rangle C_{10}H_6$, melting at 141°, is isomeric with chrysene. It is formed when its quinone is digested with zinc dust and ammonia.

Naphthanthraquinone $C_6H_4(CO)_2C_{10}H_6$, melting at 168°, is obtained from naphthoyl-o-benzoic acid $C_6H_4\langle{}^{COOH}_{CO.C_{10}H_7}$, the same as anthraquinone from benzoyl-benzoic acid (B. **19**, 2209; **29**, 827).

Naphthanthraquinone is split up by melting with potash into β-naphthoic acid and benzoic acid (B. **19**, 2209; **29**, 827; **33**, 446). **Phenanthro-anthraquinone** $C_{14}H_8(CO)_2C_6H_4$, m.p. 234°, see C. 1908, I. 1223.

Naphthacene $C_6H_4\langle{}^{CH-C-CH}_{CH-C-CH}\rangle C_6H_4$ or $C_6H_4\langle{}^{CH[2]}_{CH[3]}\rangle C_{10}H_6$, m.p. 335°, is isomeric with naphthanthracene; it is formed from its oxygen derivatives oxy- and dioxy-naphthacene-quinone by distillation with zinc dust.

Dioxy-naphthacene-quinone, *iso-ethindiphtalyl* $C_6H_4\langle{}^{C(OH)-C-CO}_{C(OH)-C-CO}\rangle C_6H_4$, m.p. 347°, red flakes, from ethindiphtalyl $C_6H_4\langle{}^{CO}_{C}\rangle O\,|\,{}^{HC=C}_{CH}\rangle O\langle{}^{C}_{CO}\rangle C_6H_4$ by transposition with sodium methylate, or by the oxidation of diketohydrindene with potassium persulphate; by oxidation with HNO_3 we obtain **naphthacene-di-quinone** $C_6H_4\langle{}^{CO.C.CO}_{CO\ C.CO}\rangle C_6H_4$, m.p. 333°, which reverts very easily into the dioxy-naphthacene-quinone; by reduction of the latter with phosphorus and HI we obtain **dihydro-naphthacene** $C_{18}H_{14}$, m.p. 207°, which with chromic acid yields **naphthacene-quinone** $C_{10}H_6(CO)_2C_6H_4$, m.p. 294°, an isomer of naphthanthraquinone (B. **31**, 1272; **33**, 446). By condensation of phthalic anhydride and α-naphthol, or of α-oxy-naphthoyl-o-benzoic acid with boric acid and sulphuric acids, we obtain **monoxy-naphthacene-quinone** $C_6H_4\langle{}^{CO[2]}_{CO[3]}\rangle C_{10}H_5[1]OH$, m.p. 303°, which, on oxidation, easily passes into the above dioxy-naphthacene-quinone, and can be converted by reduction into naphthacene and dihydro-naphthacene (B. **36**, 547, 719, 2326).

VI. Glycosides or Glucosides and Pentosides.

Glycosides or glucosides are those vegetable substances which break down into sugars, chiefly grape sugar or glucose, and other bodies, when they are exposed to the action of unorganised ferments or enzymes (1·587). Some of them decompose into iso-dulcite or rhamnose, a pentose, hence they are designated as *pentosides*. In many glycosides the exact nature of the sugar is not known. The glycosides and pentosides are therefore to be regarded as ethereal sugar derivatives. Some of them were described under their decomposition products, while many have been synthesised.

E. Fischer demonstrated that the simplest glucosides could be pre-

pared by the action of hydrochloric acid upon alcoholic sugar solutions ; they have been described in Vol. I.

A second method of forming artificial glucosides, due to Michael, is based upon the mutual action of phenols and aceto-chloro- or bromo-glucose (Vol. I.) in alkaline-alcoholic solution.

1*a*. **Sinigrin,** *potassium myronate* $C_{10}H_{18}NS_2O_{10}K=C_3H_5N:C\begin{cases}O.SO_2K\\S.C_6H_{11}O_5\end{cases}+H_2O$, m.p. 127° (anhydrous, 132°), is found in black mustard-seed and in the root of *Cochlearia armoracia*. It crystallises from water in brilliant needles. On boiling with baryta water, or by the action of the ferment myrosin, contained in mustard-seed, it is split up into d-glucose, allyl-mustard oil, and primary potassium sulphate (B. **30.** 2322).

1*b*. **Sinalbin** $C_{30}H_{44}N_2S_2O_{16}=C\begin{cases}OSO_2.O.C_{16}H_{24}NO_5\\SC_6H_{11}O_5\\N.CH_2C_6H_4OH\end{cases}+H_2O$ (?) is found in white mustard-seed. Myrosin decomposes it into glucose, sinalbin-mustard oil, and **p-oxy-benzyl-mustard oil** $SC:NCH_2C_6H_4$ [4]OH and **sinapin sulphate** $C_{16}H_{24}NO_5.HSO_4$. Sinapin easily splits up into cholin (Vol. I.) and sinapic or *oxy-dimethoxy-cinnamic acid* $(CH_3O)_2$[3, 5](OH)[4]$C_6H_2CH:CH.COOH$ (B. **30,** 2327).

A constitution resembling that of sinalbin may also be possessed by the glucosides of various cresses, such as *Tropæolum majus, Lepidium sativum,* and *Nasturtium officinale,* which, on splitting up, give benzyl-ethyl and phenyl-ethyl-mustard oil, instead of allyl-mustard oil (B. **32,** 2335).

2. **Arbutin** $C_{12}H_{16}O_7$ and **methyl arbutin** $C_{13}H_{18}O_7$ are found in the leaves of *Arbutus uva ursi.* Arbutin crystallises in fine needles, with ½–1 molecule of water, and melts at 187° (B. **16,** 800) in the anhydrous state. *Methyl arbutin* melts at 176°. It is formed artificially from arbutin by the action of methyl iodide and potash.

By their decomposition we get, besides grape sugar, hydroquinone or methyl-hydroquinone :

$$C_{12}H_{16}O_7+H_2O=C_6H_{12}O_6+C_6H_4(OH)_2.$$

3. **Salicin** $C_6H_{11}O_5.O.C_6H_4CH_2OH$, m.p. 201°, *saligenin glucose,* occurs in the bark and leaves of willows—*e.g., Salix helix*—and some poplars, from which it may be extracted with water. It can be artificially prepared by reducing helicin with sodium amalgam. It forms shining crystals, which dissolve easily in hot water and alcohol. Its taste is bitter.

Oxidants convert it into *helicin,* hence the saligenin in salicin is linked by means of the phenol-oxygen atom with the glucose. The enzymes *ptyalin* and *emulsin* (Vol. I.) decompose salicin into glucose and saligenin :

$$C_6H_{11}O_5.O.C_6H_4.CH_2.OH+H_2O=C_6H_{12}O_6+HO.C_6H_4.CH_2.OH.$$

Boiling dilute acids decompose it in a similar manner, but in so doing the saligenin is changed to saliretin.

Salicin was discovered almost simultaneously by Leroux (1830) and Buchner, and its composition was cleared up by Piria in 1845 (A. **56,** 35).

Populin, the benzoyl derivative of salicin $C_{13}H_{17}(C_7H_5O)O_7+2H_2O$,

occurs in the bark and leaves of *Populus tremula*. It can also be artificially made by the action of benzoic anhydride or benzoyl chloride upon salicin.

Helicin, salicyl-aldehyde-glucose $C_6H_4(O.C_6H_{11}O_5).CHO$, is produced by oxidising salicin with nitric acid. It reverts to salicin upon reduction. It can be artificially prepared from salicylic aldehyde and aceto-chloro-hydrose. It is broken down just like salicin by ferments or dilute acids.

Glucose-cumaraldehyde $C_6H_{11}O_5.O.C_6H_4.CH=CH.CHO$ and **Methyl-gluco-o-cumar-ketone** result from the condensation of helicin with acetaldehyde and acetone (B. **24**, 3180).

4. **Geïn** $C_6H_{22}O_7$ is found in the root of *Geum urbanum*. It splits up into glucose and eugenol (C. 1905, I. 1329).

5. **Gaultherin** $C_6H_{11}O_5O.C_6H_4COOCH_3+H_2O$ is found in numerous species of *Gaultheria* and *Spiræa*, also in *Betula lenta*, besides an enzyme "*gaultherase*," by which it is split up into glucose and salicylic methyl ester.

6. **Coniferin** $C_{16}H_{22}O_8+2H_2O$ is found in the cambium of coniferous woods, in asparagus, and in the black root of *Scorzonera hispanica* (B. **25**, 3221). It effloresces in the air, and melts at 185°. It acquires a dark-blue colour when moistened with phenol and hydrochloric acid. Boiling acids or emulsin decompose it into glucoses and *coniferyl alcohol* $C_6H_3\begin{pmatrix}O.CH_3\\OH\end{pmatrix}.C_3H_4.OH$, which is oxidised by chromic acid to :

Glyco-vanillin $C_6H_3(O.CH_3)(O.C_6H_{11}O_5).CHO$, the glucoside of vanillin, melting at 192°. Acids or emulsin split it up into glucoses and vanillin (B. **18**, 1595, 1657).

Syringin, *methoxyl-coniferin* $C_{17}H_{24}O_9+H_2O=C_6H_{11}O_5.O.C_6H_2(OCH_3)_2C_3H_4OH$, occurs in the bark of *Syringia vulgaris* and *Ligustrum vulgare*. It melts at 191° and shows changes similar to those of coniferin.

7. **Phlorizin** $C_{21}H_{24}O_{10}$, melting at 108°, occurs in the root-bark of various fruit trees; hence the name, from φλοιος, bark, and ῥιζα, root. It is intimately related to the pentosides : *naringin* and *hesperidin*. It breaks down into grape sugar and phloretin, the phloro-glucin ester of p-oxy-hydratropic acid, and the latter into phloro-glucin and phloretic acid :

$$C_{21}H_{24}O_{10}+H_2O=C_6H_{12}O_6(\text{Glucose})+C_{15}H_{14}O_5(\text{Phloretin})$$
$$C_{15}H_{14}O_5+H_2O=C_6H_6O_3(\text{Phloro-glucin})+C_9H_{10}O_3(\text{Phloretic acid}).$$

Administered internally, it produces strong glucosuria.

8. **Æsculin** $C_{15}H_{16}O_9+\frac{1}{2}H_2O$ melts at about 205° when it is anhydrous. It is found in the horse-chestnut, *Æsculus hippocastanum*, and in the root of the wild jasmine, *Gelsemium sempervirens*. Acids or ferments resolve it into glucose and æsculetine or 4, 5-dioxy-cumarin.

9. **Daphnin** $C_{15}H_{16}O_9+2H_2O$, melting at 200°, is isomeric with the preceding. It is obtained from the bark of *Daphne alpina*. It breaks down into glucose and daphnetin or 3, 5-dioxy-cumarin.

10. **Fraxin** $C_{16}H_{18}O_{10}$ occurs in the bark of *Fraxinus excelsior*, and, like æsculin, in the bark of the horse-chestnut. It decomposes into glucose and fraxetin, the monomethyl ether of a trioxy-cumarin (B. **27**, R. 130).

11. **Iridin** $C_{24}H_{26}O_{13}$, melting at 208°, occurs in the root of the violet, *Iris florentina*, etc. Dilute sulphuric acid resolves it into grape sugar and **irigenin** $C_{18}H_{16}O_8$. The latter is probably a polyoxy-ketone. Concentrated caustic alkali decomposes it into formic acid, an aromatic oxy-acid—*iridic acid* $C_{10}H_{12}O_6$, melting at 118°, which, by loss of CO_2, becomes **iridol** or 3-oxy-4, 5-dimethoxy-1-methyl-benzene, melting at 57°—and *iretol* $C_7H_8O_4$, or methoxy-phloroglucin, melting at 186° (B. **26,** 2010; **27,** R. 514).

12. **Ruberythric acid** $C_{26}H_{28}O_{14}=HO.C_{14}H_6O_2.O.C_{12}H_{11}O_3(OH)_7$, melting at 258°–260°, is the glucoside of alizarin. It is formed in the madder root of *Rubia tinctorum*, and breaks down under the influence of hydrochloric acid into alizarin and glucose (B. **20,** 2244). Purpurin is also contained in the madder root as a glucoside.

13. **Saponarin** $C_{21}H_{24}O_{12}$ is found in *Saponaria officinalis*. Boiling with dilute mineral acids splits it up into glucose and vitexin $C_{15}H_{14}O_7$. The latter, probably a flavone derivative, gives, on boiling with potash, phloro-glucin and p-oxy-aceto-phenone (C. 1906, II. 1062).

14. **Digitalin** (*Digitalinum verum*, Kiliani) $C_{35}H_{56}O_{14}$ (?) is an amorphous glucoside. It is the active principle of the digitalis glucosides, which occur in the leaves of *Digitalis purpurea* and *lutea*. Concentrated hydrochloric acid breaks it down into **digitaligenin** $C_{16}H_{22}O_2$, grape sugar $C_6H_{12}O_6$, and **digitalose** $C_7H_{14}O_5$.

Its therapeutic action consists in its occasioning "less frequent but more satisfactory heart contractions." *

The chief ingredient of the digitalis glycosides is without therapeutic action. It is crystalline **digitonin** $C_{27}H_{44}O_{13}$, which is resolved by aqueous alcoholic hydrochloric acid into **digitogenin** $C_{15}H_{24}O_4$, glucose, and galactose. The decomposition of the latter has led to a series of acids, the constitution of which is as yet undetermined (B. **27,** R. 881; **28,** R. 1056; **31,** 2454; **32,** 2201; **37,** 1215; and **43,** 3562).

From the leaves of *Digitalis purpurea* another pharmaceutically effective glucoside is obtained, called **digitoxin** $C_{34}H_{54}O_{11}$ m.p. 145°, which is split up by HCl into **digitoxose** $C_6H_{12}O_4$ (two molecules) and **digitoxigenin** $C_{22}H_{32}O_4$ (?). Besides digitoxin we find a small quantity of a yellow pigment, the so-called *digito-flavone* $C_{15}H_{10}O_6$, which belongs to the group of the flavones (*q.v.*), and is identical with luteolin (B. **32,** 2196, 1184; **34,** 3577).

15. **Saponin** $C_{32}H_{54}O_{18}$, from the root of *Saponaria officinalis*, is a white amorphous powder, which provokes sneezing and foams in aqueous solutions. Its decomposition yields glucose and sapogenin $C_{14}H_{22}O_2$ (B. **42,** 238).

16. **Convolvulin** $C_{31}H_{50}O_{16}$, from the jalapa root of *Convolvulus purga*, is a gummy mass, which is a powerful purgative. Among its decomposition products are, in addition to a sugar, **d-methyl-ethyl-acetic acid** and an **oxy-pentadecylic acid** $C_2H_5CH(CH_3).CH(OH)C_9H_{18}.CO_2H$, melting at 50°. Nitric acid oxidises the latter to methyl-ethyl-acetic acid and an acid $C_{10}H_{18}O_4$ (B. **27,** R. 885), melting at 116°, isomeric with sebacic acid (B. **27,** R. 885; C. 1901, I. 1042; II. 425, 426).

17. **Jalapin,** *scammonin* $C_{34}H_{56}O_{16}$, from *Convolvulus orizabensis*, and from scammonium resin, yields acetic acid, tiglic acid, and palmitic acid upon distillation (B. **26,** R. 591; **27,** R. 736).

* Binz, *Grundzüge der Arzneimittellehre*, p. 52.

18. **Polygonin** $C_{21}H_{20}O_5$, melting at 203°, is a glycoside, and has been obtained from the root bark of *Polygonum cuspidatum*. It yields emodin when it is decomposed with alcoholic hydrochloric acid (B. **29**, R. 86).

19. **Amygdalin**, *mandelo-nitrile diglucose* $C_{20}H_{27}NO_{11}+3H_2O : C_6H_5CH.CN$ occurs in bitter almonds and in the kernels of Pomaceæ and Amygdalaceæ, as well as in cherries, peaches, apricots, and the leaves of the cherry tree. Amygdalin crystallises from alcohol in white shining leaflets, and dissolves readily in water and hot alcohol.

History.—Amygdalin was discovered in 1830 by Robiquet and Boutron-Chalard (*A. Chim. Phys.* 2, **44**, 351). The composition and nature of amygdalin were cleared up by Liebig and Köhler (A. **22**, 1).

On boiling with dilute acids, or upon standing with water and *emulsin*, an enzyme present in bitter almonds, amygdalin, is decomposed into *oil of bitter almonds*, dextrose, and *hydrocyanic acid*.

Yeast splits off only one molecule of glucose from amygdalin, and we thus obtain **l-mandelic nitrile glucoside** $C_6H_5CH(CN).O.C_6H_{11}O_5$, m.p. 148°, which is decomposed by emulsion with intermediate formation of d-mandelic nitrile into benzaldehyde, prussic acid, and d-glucose, and, on saponification with concentrated HCl, yields *l-mandelic acid*, together with glucose and ammonia (B. **28**, 1508). For *lauro-cerasin*, see C. 1885, 570. Other glucosides are **prulaurasin** (C. 1907, II. 1340), **sambunigrin** (C. 1907, II. 69), **durrhin, linamarin,** and **virianin.**

Pentosides, Rhamnosides.—The following pentosides are to be regarded as ethereal compounds of *rhamnose* $C_6H_{14}O_6=C_6H_{12}O_5+H_2O$ (I. 536), or of iso-dulcite :

1. **Naringin** $C_{21}H_{26}O_{11}+4H_2O$, melts when anhydrous at 170°. It is found chiefly in the blossoms and also in other parts of the tree *Citrus decumana* of Java. The name of the pentoside is derived from " naringi," a Sanscrit word meaning orange. Dilute acids decompose it into rhamnose and *naringenin*, melting at 230°. The latter is the phloro-glucin ether of p-oxy-cinnamic acid, which concentrated caustic potash breaks down into phloro-glucin and p-cumaric acid (B. **20**, 296) :

$$C_{21}H_{26}O_{11} = C_6H_{14}O_6 \text{ (Rhamnose)} + C_{15}H_{12}O_5 \text{ (Naringenin)}$$
$$C_{15}H_{12}O_5+H_2O=C_6H_6O_3 \text{ (Phloro-glucin)}+C_9H_8O_3 \text{ (p-Cumaric acid).}$$

2. **Hesperidin** $C_{50}H_{60}O_{22}$ (?), melting at 251°, is present in unripe oranges, lemons, etc. It decomposes, when heated, into glucose, rhamnose, and hesperetin, melting at 226°. Caustic potash resolves the latter into phloro-glucin and iso-ferulic acid (B. **14**, 948) :

$$C_{50}H_{60}O_{27}+3H_2O=2C_6H_{12}O_6+C_6H_{14}O_6 \text{ (Rhamnose)}+2C_{16}H_{14}O_6 \text{ (Hesperetin).}$$
$$C_{16}H_{14}O_6 + H_2O=C_6H_6O_3 \text{ (Phloro-glucin)}+C_{10}H_{10}O_4 \text{ (Iso-ferulic acid).}$$

3. **Quercitrin** $C_{21}H_{22}O_{12}$ is present in the bark of *Quercus tinctoria*, and is applied under the name quercitrone as a yellow dye. It breaks down into rhamnose and quercetrin (see this), a phenyl-benzo-pyrene derivative (B. **26**, R. 234 ; **28**, 2303) :

$$C_{21}H_{22}O_{12}+H_2O=C_6H_{14}O_6 \text{ (Rhamnose)}+C_{15}H_{10}O_7 \text{ (Quercetrin).}$$

4. **Frangulin** $C_{21}H_{20}O_9$, melting at 286°, occurs in the bark of *Rhamnus frangula.* When it is saponified with alcoholic hydrochloric acid rhamnose, *emodin* and a trioxy-methyl-anthraquinone, isomeric with the latter, are produced (B. **25,** R. 370) :

$$C_{21}H_{20}O_9+2H_2O=C_6H_{14}O_6 \text{ (Rhamnose)}+C_{15}H_{10}O_5 \text{ (Emodin).}$$

5. **Aloin.**—Several apparently different aloins : aloin, barbaloin, nataloin, are found in aloes, the dried juice of various species of aloe. The best known is **barbaloin,** isolated from Barbadoes aloes, occurring in yellowish needles, $C_{14}H_5O_2(OH)_2CH_2.O.C_6H_{11}O_4$ (?) (C. 1909, II. 622). On heating with aqueous alcoholic HCl it is split up into an aldopentose (osazone, m.p. 209°) and aloe-emodin, and therefore shows the same transformations as the latter (C. 1910, I. 104). Chromic acid oxidises it to rhein, a dioxy-anthraquinone-carboxylic acid (above) ; with HNO_3 **chrysamic acid** is obtained, and the so-called **aloetic acid,** probably a mixture of several highly nitrated aloe-emodins.

VII.—Bitter Principles.

Under the head of " bitter principles," or indifferent substances, is embraced a class of vegetable bodies many of which have already found their place in the chemical system. Those yet uninvestigated are :

Cantharidin $C_{10}H_{12}O_4$, melts at 218° and sublimes readily. It is contained in Spanish flies and other insects. It tastes very bitter, and produces blisters on the skin. It dissolves when heated with alkalies and forms salts of *cantharinic acid* $C_{10}H_{14}O_5$. It combines with phenylhydrazin to an *addition product* $C_{16}H_{20}N_2OH$, melting at 194°, and a *phenyl-hydrazone,* melting at 238° (B. **26,** 140). Cantharidin is probably a lactone-carboxylic acid. Hydriodic acid converts cantharidin into *cantharic acid* $C_{10}H_{12}O_4=C_8H_{11}O.CO.CO_2H$, isomeric with it. When this acid is distilled with lime, *cantharene* or *dihydro-o-xylene* results.

Anemonin $C_{10}H_8O_4$, m.p. 150°, appears to be closely related to cantharidin. It is a crystalline constituent of the extracts of nearly all *Anemones* and *Ranunculaceæ* (M. **20,** 634).

Picro-toxin $C_{15}H_{16}O_6+H_2O$ is found in the grains of cockle, and crystallises in fine needles, melting at 201°. It has an extremely bitter taste, and is very poisonous.

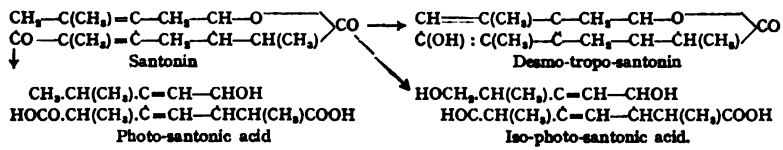
It is a mixture of two bodies : **picro-toxinin** $C_{15}H_{16}O_6+H_2O$, m.p. 201°, and **picrotin** $C_{15}H_{18}O_7$, m.p. 249°, which are best separated by bromination in aqueous solution. In this case only the picro-toxinin is brominated to sparingly soluble bromo-picro-toxinin, which can then be reduced to picro-toxinin ; the latter is a strong reducing agent, contains two hydroxyl groups, and seems to be a lactone (B. **31,** 2958).

Santonin $C_{15}H_{18}O_3$, melting at 170°, $[\alpha]_D=-171{\cdot}37°$, is the active principle of **artemisia cina.** It dissolves in alkalies to salts of **santonic acid** $C_{15}H_{20}O_4$, which breaks down at 120° into water and santonin. On boiling with baryta water we obtain salts of isomeric **santoic acid** $C_{15}H_{20}O_4$, which melts at 171°.

This acid, upon further oxidation, yields a tetracarboxylic acid. For its constitution, see B. **29,** R. 1119. Santonin is a lactone. It

bears the same relation to santonic and santoic acids as cumarin to cumarinic and cumaric acids. Again, it contains the ketone group; its *phenyl-hydrazone* melts at 220°. When santonin is reduced with hydriodic acid or with stannous chloride and hydrochloric acid, *santous acid* $C_{15}H_{20}O_3$ results. This is dextro-rotatory and melts at 179°. The corresponding lævo-rotatory modification and the (d+l)-acid are known. When these three acids are fused with caustic potash, propionic acid, dimethyl-β-naphthol, and hydrogen are produced. Hence it would seem that santonin is a derivative of a *hexahydro-dimethyl-naphthalene* (B. **27,** 530; **28,** R. 392; **29,** R. 291, 296). When santonin is reduced with tin and hydrochloric acid, not only santous acid is formed, but also a hydrocarbon $C_{10}H_{13}(CH_3)_2(C_2H_5)$, boiling at 248°, which probably is dimethyl-ethyl-octohydro-naphthalene (B. **28,** R. 622).

By heating with mineral acids under various conditions santonin is converted into diverse so-called **desmo-tropo-santonins** $C_{15}H_{18}O_3$, distinguished by their optical rotatory power, and from santonin by the absence of the ketone reaction and the presence of phenol reactions. It is therefore assumed that there is a transformation of a ketone form into a phenol form, as in the case of carvone and carvacrol (B. **31,** 3131; **36,** 1386, 2667). Other transformations are produced by sunlight. In an acetic acid solution the two-basic so-called **photo-santonic acid** $C_{15}H_{22}O_5$ is formed together with **iso-photo-santonic acid,** a dioxaldehyde-carboxylic acid; the former passes into dehydro-photo-santonic acid $C_{15}H_{20}O_4$, with loss of water, which on oxidation yields **dimethyl-phthalide-carboxylic acid** $O\langle^{C(CH_3)_2[2]}_{CO[2]}\rangle C_6H_3[5]COOH$, and on distillation of its Ba-salt 1, 5, 2-diethyl-iso-propyl-benzol (C. 1902, I. 1402). From these data the following formulæ have been deduced:



Artemisin $C_{15}H_{18}O_4$, from the seeds of *Artemisia maritima,* is a lactone closely related to santonin (cp. B. **34,** 3717; C. 1905, I. 98).

VIII.—Natural Dyes.

The important natural dyes, *indigo, alizarin,* and its allies, *euxanthic acid, gentisin,* etc., have found their place in the system of organic chemistry. The following are some of the natural dyes which have not yet been investigated:

Brasilin $C_{16}H_{14}O_5$ is found in Brazil-wood and red-wood; crystallises with $1\frac{1}{2}H_2O$ in white, shining needles, and dissolves in alkalies with a carmine-red colour on exposure to the air. Acids then precipitate *brasileïn* $C_{16}H_{12}O_5+H_2O$ from the solution. The action of iodine upon brasilin also produces this compound. It can be reconverted into brasilin by reduction, best by way of its acetyl compound (B. **36,** 3951; M. **25,** 871). Brasileïn is, therefore, related to brasilin as dyes are related to leuco-bodies. Brasilin forms mono-, di-, tri-, and tetra-alkyl ethers (B. **27,** 524; R. 304; **29,** R. 219); while brasileïn

forms, besides the normal di- and trialkyl ethers, tri- and tetra-alkyl brasileinols, with attachment of one molecule H_2O (C. 1908, II. 609). On distillation, brasilin yields much resorcin. On conducting air for some time through a strongly alkaline solution of brasilin, we obtain a compound $C_9H_6O_4$ which probably has the constitution $C_6H_3(OH)\begin{cases}[1]O—CH\\[2]CO—C(OH)\end{cases}$, since its dimethyl ether is split up by sodium alcoholate into formic acid and **fisetol-dimethyl ether** $C_6H_3[5](OCH_3)\begin{cases}[1]OH\\[2]COCH_2(OCH_3)\end{cases}$, a decomposition product of fisetin (B. **32**, 1024). Oxidation of **trimethyl-brasilin** $C_{16}H_{10}O(OH)(OCH_3)_3$, m.p. 140°, with MnO_4K, on the other hand, produces various acids, among which may be mentioned **5-methoxy-phenoxy-aceto-2-carboxylic acid** $(CH_3O)C_6H_3\begin{cases}OCH_2COOH\\COOH\end{cases}$, **4, 5-dimethoxy-phenyl-aceto-2-carboxylic acid** $(CH_3O)_2C_6H_2\begin{cases}CH_2CO_2H\\CO_2H\end{cases}$, and **m-hemipinic acid** $(CH_3O)_2C_6H_2(COOH)_2$, also **brasilic acid** $(CH_3O)C_6H_3\begin{cases}O—CH_2\\CO.C(OH).CH_2COOH\end{cases}$ and **brasilinic acid** $(CH_3O)C_6H_3\begin{cases}O.CH_2CO_2H\\CO.C_6H_2(OCH_3)_2CO_2H\end{cases}$.

This last acid is also formed by the condensation of m-hemipinic anhydride with m-methoxy-phenoxy-acetic ester by means of $AlCl_3$. In a similar manner, the **anhydro-brasilic acid** $C_{12}H_{10}O_5$ obtained from brasilic acid by dehydration has been prepared synthetically (C. 1908, I. 1698). On oxidising trimethyl-brasilin with chromic acid, we obtain a ketone, **trimethyl-brasilone** $C_{19}H_{18}O_6$, which is converted by HNO_3 into **nitro-hydroxy-dihydro-trimethyl-brasilone** $C_{19}H_{19}O_7(NO_2)$. This can be split up by alkalies into **methoxy-salicylic acid** $(CH_3O)C_6H_3(OH)COOH$ and **nitro-homo-veratrol** $NO_2C_6H_2(CH_3)(OCH_3)_2$. The trimethyl-brasilone easily passes into **trimethyl-dehydro-brasilone** $C_{19}H_{16}O_5$, with loss of H_2O, and this behaves precisely like a derivative of β-naphthol. With diazonium solutions it couples up to azo-dyes; with HNO_3 it forms a nitro-compound, from which, by successive reduction and oxidation, an o-quinone corresponding to β-naphthoquinone is obtained, known as **trimethoxy-α-brasane-quinone** $C_{19}H_{14}O_6$ (C. 1909, I. 1569). By treatment with HI and with concentrated H_2SO_4, trimethyl-brasilone is isomerised, and appears to pass into derivatives of **ββ-phenylene-naphthylene oxide** (brasane) (C. 1902, II. 746; **35**, 1609; **36**, 2193; **37**, 631; M. **23**, 165).

Hæmatoxylin $C_{16}H_{14}O_6+3H_2O$ is the colouring-matter of logwood (*Hæmatoxylon campechianum*), is very soluble in water and alcohol, and crystallises in yellowish prisms having a sweet taste. It dissolves in alkalies with a violet-blue colour. The importance of logwood lies in the production of bluish-black shades by means of iron and chromium. Distillation, or fusion with potash, produces pyrogallic acid from hæmatoxylin (B. **36**, 1561). When distilled or fused with potassium hydroxide, pyrogallic acid and resorcinol result from it. If the ammonium hydroxide solution be allowed to stand exposed to the air, there results **hæmatein-ammonia** $C_{16}H_{11}(NH_4)O_6$, from which acetic acid precipitates the free **hæmatin** $C_{16}H_{12}O_6$ (at 120°), a reddish-brown body, which has metallic lustre after drying (A. **216**, 236). It yields penta-ethyl- and penta-acetyl ethers. In the oxidation of tetra-

methyl-hæmatoxylin with MnO_4K, acids are obtained analogous to those from the oxidation of trimethyl-brasilin, *e.g.* **dimethoxy-phenoxy-acetic-o-carboxylic acid** $(CH_3O)_2C_6H_2\{^{[1]OCH_2COOH}_{[2]COOH}$, meta-hemipinic acid, and the hæmatoxylinic acid corresponding to brasilinic acid (above). Similarly, tetramethyl-hæmatoxylin on oxidation with CrO_3 yields tetramethyl-hæmatoxylone, corresponding to trimethyl-brasilone, and giving quite similar decomposition products (C. 1902, II. 750; B. **86,** 2202). Hæmatoxylin is therefore only distinguished from brasilin by the entry of an HO group into the benzene nucleus. From the data hitherto obtained, Perkin has deduced the following formulæ for brasilin and hæmatoxylin:

$$HO[5]C_6H_3\left\{\begin{matrix}[1]O.CH_2.C(OH).CH_2[1] \\ [2]\text{———}CH\text{———}[2]\end{matrix}\right\}C_6H_3[4,5](OH)_2$$

Brasilin.

$$(HO)_2[5,6]C_6H_3\left\{\begin{matrix}[1]O.CH_2.C(OH).CH_2[1] \\ [2]\text{———}CH\text{———}[2]\end{matrix}\right\}C_6H_3[4,5](OH)_2$$

Hæmatoxylin.

Carthamin $C_{14}H_{16}O_7$ occurs in safflower, the blossoms of *Carthamus tinctorium*, and is precipitated from its soda solution by acetic acid as a dark-red powder, which, on drying, acquires a metallic lustre. It dissolves with a beautiful red colour in alcohol and the alkalies. It yields para-oxy-benzoic acid with caustic potash (A. **186,** 117). On boiling with dilute potash it forms p-cumaric acid and p-oxy-benzaldehyde (C. 1910, II. 805).

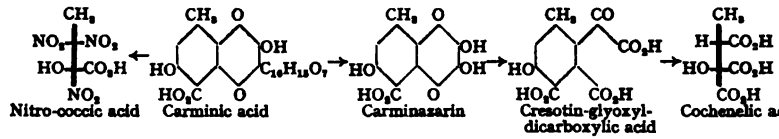
Curcumin $C_{21}H_{20}O_6=[CH_3O[3]OH[4]C_6H_3CH:CH.CO]_2CH_2(?)$, m.p. 183°, the dyestuff of the curcuma root of *Curcuma longa* and *viridiflora*, crystallises in orange prisms and dissolves in alkalies to form reddish-brown salts. It yields a *dimethyl ether* $C_{21}H_{18}O_4(OCH_3)_2$, m.p. 137°, and a *diacetyl compound* $C_{21}H_{18}O_6(C_2H_3O)_2$ (C. 1911, I. 652). With hydroxyl-amine we obtain, according to conditions, an oxime $C_{21}H_{21}O_6N$, m.p. 162°, or an isoxazol derivative $C_{21}H_{19}O_5N$, m.p. 173°. On heating with potash it forms ferulic acid (B. **48,** 2163).

Lichen dyes (*J. pr. Ch.* 2, **58,** 465; A. **306,** 282; **310,** 230), compare orseille, litmus, vulpinic acid. Of the numerous substances contained in lichens, **usnic acid** $C_{18}H_{16}O_7$, occurring in *usnea* and many other species, has been studied in detail. The acid is optically active, and is found naturally in the antipodic forms $[\alpha]_D=\pm 49{\cdot}5°$, m.p. 203°, and in the racemic form, m.p. 192°. It forms an oxime, an oxime anhydride, and a semi-carbazone, and is therefore probably a ketonic acid.

On oxidation it is completely burnt to CO_2, oxalic acid, and acetic acid; it therefore contains no aromatic nucleus; by gentle oxidation with MnO_4K the *di-basic usnonic acid* is obtained, $C_{18}H_{16}O_8$. On heating with alcohols to 150°, usnic acid splits off CO_2, takes up H_2O, and forms *dibasic decarbo-usnic acid* $C_{17}H_{18}O_6$. For its constitutional formula, see A. **310,** 281; **324,** 139.

Carminic acid $C_{11}H_{12}O_7$ is found in cochineal, from *Coccus cacti coccinelliferi*, an insect peculiar to different cactus varieties. It is a purple-red mass, dissolving readily in water and alcohol, which forms red salts with the alkalies. Cochineal is applied in wool-dyeing for the production of scarlet-red colours. This application has diminished

very greatly since the discovery of the red azo-dyes, like *Bieberich scarlet* and others. The constitution of carminic acid is not yet fully elucidated (B. **42**, 1611). Potassium permanganate oxidises it to a **methyl-trioxy-α-naphtho-quinone-carboxylic acid** $C_{12}H_{17}O_7$, which, in its behaviour, closely resembles iso-naphthazarin, and is therefore called **carminazarin.** On oxidation with HNO_3 it yields a tetraketone, **carminazarin-quinone** $C_{12}H_6O_7+2H_2O$, and in alkaline solution it is converted by atmospheric oxygen into a cresotin-glyoxyl-dicarboxylic acid $C_{11}H_8O_8+2H_2O$, which, on heating with concentrated H_2SO_4, decomposes into CO and the so-called **cochinelic acid** $C_{10}H_8O_7$. This acid, first obtained by the direct oxidation of carminic acid with potassium persulphate, is probably an m-cresol-4, 5, 6-tricarboxylic acid, since, on heating with water, it yields oxy-uvitinic acid (α-coccinic acid), and 1, 3, 5-cresotinic acid, and on heating alone, oxy-methyl-o-phthalic acid (B. **30**, 1731). By boiling with HNO_3, carminic acid is converted into **nitro-coccic acid** or symmetrical trinitro-cresotinic acid. The following formulæ illustrate this demolition of carminic acid :



The action of bromine upon carminic acid takes place in several stages. A *dibromo-hydro-bromide* $C_{22}H_{20}Br_2O_{13}.HBr$ is first formed. This, on heating, easily splits off HBr and CO_2, and passes into *decarboxy-dibromo-carminic acid* $C_{21}H_{20}Br_2O_{11}$. By strong action of bromine, several so-called bromo-carmines are formed : **α-bromo-carmine,** a derivative of diketo-hydrindene $HO(CH_3)C_6Br_2\langle{}^{CO}_{CO}\rangle CBr_2$, which, on heating with soda solution, decomposes into bromoform and dibromoxy-methyl-phthalic acid, and **β-bromo-carmine** $C_{11}H_6Br_2O_6$, probably a naphtho-quinone derivative (B. **43**, 1363). On methylating carminic acid we obtain, according to the conditions, various methyl derivatives, including **carminic acid hexamethyl ether** $C_{22}H_{16}(CH_3)_6O_{13}$ (B. **42**, 1922). Closely related to carminic acid is :

Kermessic acid $C_{18}H_{12}O_9$, red needles, m.p. 250° with decomposition, from the insect *Lecanium Ilicis.* Oxidation with HNO_3 gives nitro-coccic acid in this case also. Its dimethyl ether yields, with MnO_4K, methyl-cochenilic methyl ester, as well as the dimethyl ether of cresotin-glyoxyl-dicarboxylic acid (B. **43**, 1387). Compare also the similarly constituted **laccainic acid** $C_{16}H_{12}O_8$ (B. **29**, 1285).

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